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KINETIC ENERGY RELEASE AND POSITION OF THE TRANSITION STATE DURING THE INTRAMOLECULAR SUBSTITUTION OF IONIZED BENZALACETONES *

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ABSTRACT

The formation of 2-methylbenzopyrylium ions 3^+ by intramolecular substitution of various ortho substituents in the molecular ions of benzalacetones 1 requires a constant activation energy of 0.5—0.6 eV. Consequently the reverse reactions have different activation energies $\epsilon_r^\ddagger$, which depend on the nature of the substituent. The heat of formation of 3^+ was determined and $\epsilon_r^\ddagger$ evaluated. Measurement of the kinetic energy release T_B gives the energy-partitioning ratios $q = T_B/\epsilon_r^\ddagger$, which form two groups in the ranges 0.2—0.3 and 0.9—1.0. The group with q = 0.2—0.3 corresponds to the class of exothermic reactions and that with q = 0.9—1.0 to the class of endothermic (thermoneutral) processes. The large change in q, paralleling the change in reaction enthalpy, is interpreted as an alteration in the position of the transition state. The results show that some of Polanyi's concepts in the field of reaction dynamics as well as a recently developed "quantitative Hammond-postulate" are also followed by complicated organic species.

INTRODUCTION

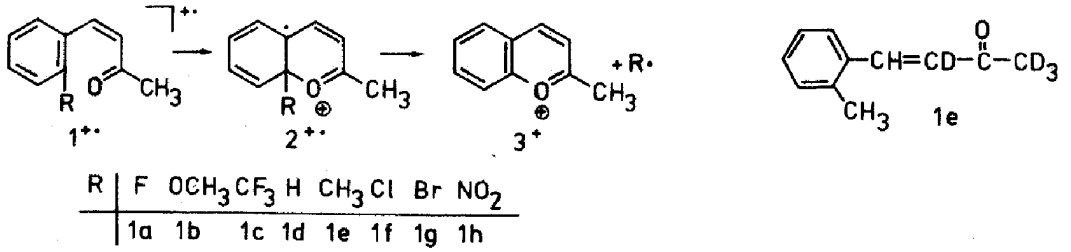
One important topic of research in the dynamics of elementary chemical reactions is the partitioning of the excess energy of an activated complex among the degrees of freedom of the reaction products. The experimental methods employed in the field of bimolecular reactions mainly comprise molecular-beam experiments [2], measurements of infrared-chemiluminescence [3], reactions of chemically activated species [4] as well as ion—molecule reactions [5].

With the development of newer mass-spectrometric techniques [6] it is now also possible to determine the energy partitioning in unimolecular reactions of complicated ions [7]. These studies might therefore provide an answer to the question of whether the results obtained in the more fundamental experiments involving small molecules, and the corresponding theoretical interpretations [8], are also valid in the case of large, polyatomic organic

* Ref. 1.

ions. If this were so it would forge a link between these reaction-dynamical concepts and the mechanistic models proposed for organic reactions.

It has been shown previously [1] that the molecular ions of benzalacetone, 1d, and some *ortho*-, *meta*- and *para*-substituted derivatives lose a hydrogen atom or substituent during the course of an intramolecular aromatic substitution reaction to yield 2-methylbenzopyrylium ions, 3 (see Reaction 1).



R	F	OCH_3	CF_3	H	CH_3	Cl	Br	NO_2
	1a	1b	1c	1d	1e	1f	1g	1h

Reaction 1

The results of a closer inspection of the energetics of this reaction using benzalacetone and some *ortho*-substituted derivatives, **1a—1h** (see above) are reported in this paper. It appears that the kinetic energy released during the substitution reaction can be explained on the basis of a recent "quantitative Hammond-postulate" [9] and also by some of Polanyi's concepts in reaction dynamics [8].

RESULTS

Figure 1 represents the schematic reaction profile for a direct substitution reaction and defines some energy data together with the symbols employed.

The experimentally determined energy data for the intramolecular substitution of ionized benzalacetones, $1^{+\cdot}$, are summarized in Table 1, together with some further values derived from these data.

The experimental activation energy for the forward reaction $\epsilon_h^\ddagger$ is given as the difference between the appearance energy $A(3^+)$ of ions 3^+ and the ionization energy $I(1)$ of benzalacetones, 1. Surprisingly, $\epsilon_h^\ddagger$ is constant in the series of compounds 1a—1g and does not increase with increasing dissociation energy D of the bond to be broken during the reaction (last row in Table 1). A slight increase of $\epsilon_h^\ddagger$ with increasing D has been observed in similar aromatic substitution reactions [10]. The activation energy for the reverse reaction, $\epsilon_r^\ddagger$, is given (Fig. 1) by

$$\epsilon_r^\ddagger = \epsilon^* + T_B = \epsilon_h^\ddagger - \Delta H_R^+ \quad (1)$$

which can also be derived from

$$\epsilon_r^\ddagger = A(3^+) + \Delta H_f(1) - \Delta H_f(3^+) - \Delta H_f(R^\cdot) \quad (2)$$

It follows from eqn. (1) that $\epsilon_r^\ddagger$ depends directly on the heat of reaction,

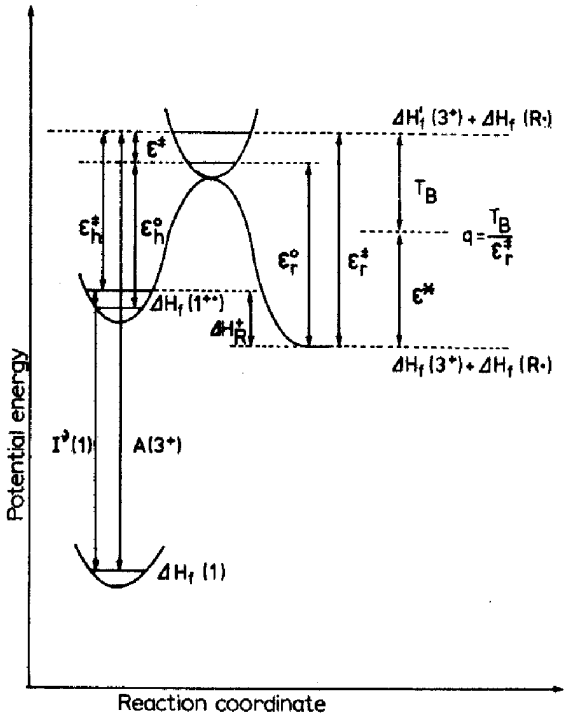


Fig. 1. Schematic energy profile for a direct substitution reaction $1^{+\cdot} \rightarrow 3^+ + R$ in weakly excited ions $1^{+\cdot}$.
$I^V(1)$ = vertical ionization energy of compounds 1; $A(3^+)$ = appearance energy of ions 3^+ from 1; ΔH_f = heats of formation; $\Delta H_f'$ = apparent heat of formation; ΔH_R^+ = experimental heat of reaction; T_B = maximum kinetic energy released; $\epsilon_h^‡$ = experimental activation energy for the forward reaction; ϵ_h^0 = minimum activation energy for the forward reaction; $\epsilon_r^‡$ = experimental activation energy for the reverse reaction; ϵ_r^0 = minimum activation energy for the reverse reaction; $\epsilon^‡$ = statistical excess energy of the activated complex; ϵ^* = internal excitation energy of the products.

ΔH_R^+, as $\epsilon_h^‡$ has been shown to be constant. Thus, in order to find out how much of $\epsilon_r^‡$ appears as translational energy, T_B, of the products, the heat of formation of 2-methylbenzopyrylium ions, 3^+, and the kinetic energy release must be determined. The latter values can easily be obtained from the widths of the appropriate signals in the MIKE spectra [11] of the molecular ions of the benzalacetones. It is more difficult to determine a value for $\Delta H_f(3^+)$, however, as no gas-phase heats of formation for pyrylium ions have been published; the $A(3^+)$ data of Table 1 can be used only with caution, since the activation energies for the reverse reactions, $\epsilon_r^‡$ are unknown.

Heat of formation of ions 3^+

It follows from eqn. (2) that reliable heats of formation can be determined from appearance energy data only if $\epsilon_r^‡$ is negligible. In contrast to many simple bond cleavage reactions, $\epsilon_r^‡$ must be taken into account since new bonds are formed during the reaction. The appearance energies $A(3^+)$

TABLE 1

Energy data [a] relating to the intramolecular substitution in ionized *ortho*-substituted benzalacetones, $1^{+\cdot}$, yielding 2-methylbenzopyrylium ions 3^+

Variable	1a R = F	1b OCH_3	1c CF_3	1d H	1e CH_3	1f Cl	1g Br	1h NO_2	4 CH_3
$I(1)$	8.9	8.2	9.0	8.8	8.5	8.8	8.7	— [b]	7.8
$A(3^+)$	9.5	8.7	9.6	9.4	9.1	9.3	9.2	9.4	8.8
$\epsilon_h^{\ddagger} = A(3^+) - I(1)$	0.6	0.5	0.6	0.6	0.6	0.5	0.5	(0.2) [c]	1.0
$\Delta H_f(1)$	−2.21	−1.86	−7.30	−0.26	−0.56	−0.56	+0.04	−0.43	−0.43
$\Delta H_f(R^{\cdot})$	0.82	0.15	−4.55	2.26	1.47	1.26	1.16	0.34	1.47
$\Delta H_f'(3^+)$	6.4_7	6.6_9	6.8_5	6.8_8	7.0_7	7.4_8	8.0_8	8.6_3	6.9_0
T_B	0.10	0.17	0.47	0.52	0.61	0.35	0.39	0.48	0.26
$\Delta H_f'(3^+) - T_B$	6.3_7	6.5_2	6.3_3	6.3_6	6.4_6	7.1_3	7.6_9	8.1_5	6.6_4
$\epsilon_r^{\ddagger}$ [d]	0.1	0.3	0.5	0.5	0.7	1.1	1.7	2.2	0.5
$q = T_B/\epsilon_r^{\ddagger}$	1.0 [e]	0.6 [e]	0.9	1.0	0.9	0.3	0.2	0.2	0.5
$\Delta H_f(1^{+\cdot})$	6.69	6.34	1.70	8.54	7.94	8.24	8.74	(8.49) [c]	7.37
$\Delta H_R^{\ddagger}$ [d]	$+0.5_3$	$+0.2_1$	$+0.1_5$	$+0.1_2$	-0.0_7	-0.5_8	-1.1_8	-1.7_5 [c]	
$X_0^{\ddagger}$ [e]	0.8_6	0.6_3	0.6_0	0.5_5	0.4_6	0.3_1	0.2_3	(0.09) [c]	
ΔD [f]	+0.41	+0.09	+0.03	0.00	−0.19	−0.70	−1.30	−1.87	

[a] In eV.
[b] $M^{+\cdot}$ intensity too low.
[c] With I (*p*-nitrobenzalacetone) = 9.2 eV.
[d] With $H_f(3^+)$ = 6.4 eV.
[e] See discussions.
[f] Dissociation energy of the phenyl—substituent bond relative to $D(1d^{+\cdot})$; see footnote p. 275 and text.

therefore initially give apparent heats of formation, $\Delta H_f'(3^+)$, which provide upper limits for $\Delta H_f(3^+)$.

$$\Delta H_f'(3^+) = \Delta H_f(3^+) + \epsilon_r^\ddagger \quad (3)$$

The $\Delta H_f'(3^+)$ data in Table 1 show a large range of values (6.5—8.6 eV), the variation being considerably greater than the experimental error for the determination of $A(3^+)$ *. The MIKE spectra of the ions 3^+ generated from the benzalacetones, 1a—1h, show that all these ions possess identical structures, thus demanding a single value for $\Delta H_f(3^+)$. The different apparent heats of formation therefore reflect directly the different activation energies for the reverse reaction (see eqn. 3).

According to eqn. (2), $\epsilon_r^\ddagger$ depends on the heat of reaction, being smallest in case of the most endothermic and largest in case of the most exothermic reaction (assuming that $\epsilon_h^\ddagger$ is constant or varies only slightly). The heat of reaction, in turn, depends directly on the different dissociation energies, D, of the bonds being broken (vide infra); a relationship should therefore exist between the apparent heats of formation and the bond-dissociation energies, D.

Figure 2 shows the relationship between the apparent heats of formation $\Delta H_f'(3^+)$ and the relative bond-dissociation energies ΔD **. The resulting straight line confirms that $\Delta H_f'(3^+)$, and therefore $\epsilon_r^\ddagger$, is inversely proportional to the bond-dissociation energy for the benzalacetones studied. Accordingly the apparent heats of formation bear more relation to the real values when determined from those benzalacetones with the most strongly bound substituents. Nevertheless, the exact magnitude of $\epsilon_r^\ddagger$ remains unknown.

The next step towards the real value for $\Delta H_f(3^+)$ is taken in determining the fraction of $\epsilon_r^\ddagger$ released as kinetic energy if the activated complex collapses to the products 3^+ and R. The kinetic energies are released in various distributions [7f] which can be determined by an analysis of the shapes of the metastable ion decomposition peaks [6]. In order to correct $\Delta H_f'(3^+)$ for $\epsilon_r^\ddagger$, however, only the maximum values of the kinetic energies T_B are required. These can be approximated from the base-widths of the respective signals in the MIKE spectra of compounds 1. It can be seen from Table 1, that, in the case of compounds 1a and 1b, which have the most firmly-bonded substituents (R = F and R = OCH_3), relatively small T_B values (0.10 and 0.17 eV) are found. This observation is in agreement with Fig. 2, which postulates the smallest value of $\epsilon_r^\ddagger$ for compounds 1a and 1b. For compounds 1c—1e (R = CF_3, H and CH_3) the T_B values rise to 0.5—0.6 eV in

* This variation cannot be attributed to the different amounts of statistical excitation energy, ϵ^+, possessed by the activated complexes, as $\epsilon^\ddagger$ has been estimated not to exceed 0.1—0.3 eV [12].

** As the heat of formation of the ion 5^+ (see Reaction 3) is not known, the dissociation energies have been calculated relative to the unsubstituted ionized 1d as $\Delta D = \Delta H_f(R^\cdot) - \Delta H_f(H^\cdot) + \Delta H_f(1d^{+\cdot}) - \Delta H_f(1^{+\cdot})$.

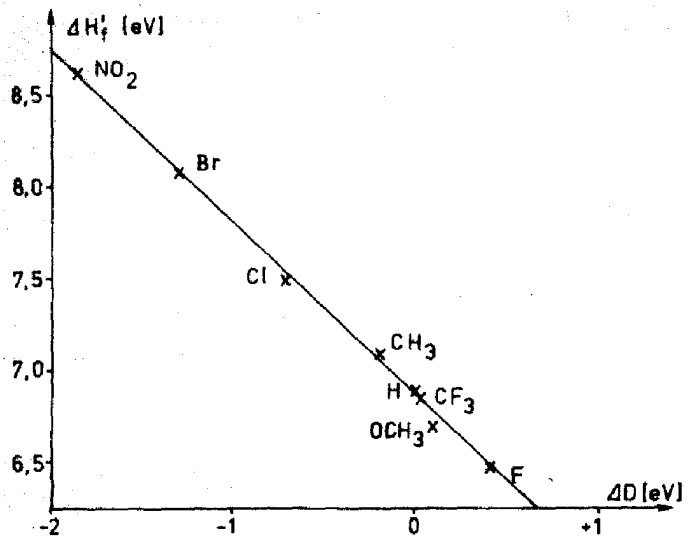
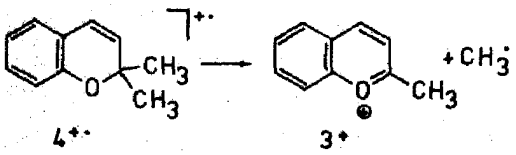


Fig. 2. Correlation between the apparent heat of formation $\Delta H_f^\circ(3^+)$ and the relative dissociation energy of the bond being broken during the reaction $1^{+\cdot} \rightarrow 3^+ + R$.

accord with the predicted increase in $\epsilon_r^\ddagger$. This trend is interrupted, however, at compound 1f(R = Cl), where T_B decreases to 0.35 eV despite the further increase in $\epsilon_r^\ddagger$. T_B increases again slightly for compounds 1g and 1h, (R = Br, NO_2), but not as much as the large increase in $\epsilon_r^\ddagger$ might have led one to expect.

Correction of the apparent heats of formation using the maximum kinetic energy release leads to an approximately constant value of 6.4 ± 0.1 eV for the corrected heat of formation of ions 3^+ from compounds 1a—1e. For compounds 1f—1h, however, the correction leads to much higher and more scattered values (7.1—8.2 eV), indicating that they must contain large, random contributions of $\epsilon_r^\ddagger$.

In order to obtain $\Delta H_f(3^+)$ independently of the aromatic substitution reaction under investigation, the appearance energy of ions 3^+ generated from 2,2-dimethylchromene, 4 (see Reaction 2) was determined.



Reaction 2

After correcting T_B for the CH_3-elimination from 4, a value $\Delta H_f(3^+) = 6.6$ eV is obtained (see Table 1). Although the loss of a CH_3 radical from $4^{+\cdot}$ corresponds to a direct bond cleavage, the signal for CH_3-elimination from metastable $4^{+\cdot}$ is broadened and clearly deviates from a Gaussian shape. This indicates that the reverse reaction has a considerable activation energy. Since the

back-reaction corresponds to the addition of a methyl radical to a pyrylium ion, thereby destroying its aromatic character, these findings are quite reasonable. However, these considerations show that reverse activation energies can be expected when generating pyrylium ions from pyranes, thus leading to values for the heat of formation of pyrylium ions which are too high. Nevertheless, the value of $\Delta H_f(3^+)$ (6.6 ± 0.2 eV) obtained from compound **4** is only a little larger than the value (6.4 ± 0.1 eV) derived from the five compounds **1a**—**1e**. This confirms that the true value for $\Delta H_f(3^+)$ must be very close to 6.4 eV. This is therefore the value used in the following calculations *.

Energy partitioning for $1^{+\cdot} \rightarrow 3^+ + R^\cdot$

With a knowledge of $\Delta H_f(3^+)$, the heats of reaction, ΔH_R^+, can be calculated using eqn. (3) (see Table 1).

$$\Delta H_R^+ = \Delta H_f(3^+) + \Delta H_f(R^\cdot) - I(1) - \Delta H_f(1) \qquad (3)$$

It is evident that the intramolecular substitution reactions are endothermic or nearly thermoneutral for compounds **1a**—**1e** and exothermic for compounds **1a**—**1e**. This result will be discussed later.

The reverse activation energies, $\epsilon_r^\ddagger$, can now be calculated from eqn. (1) or (2) (see Table 1). For the most endothermic reaction, that of $\mathbf{1a}^{+\cdot}$ (R = F), $\epsilon_r^\ddagger$ is small and probably consists of the freely fluctuating excess energy of the activated complex, $\epsilon^\ddagger$. The peak corresponding to the decomposition of metastable $\mathbf{1a}^{+\cdot}$ is therefore sharp and Gaussian in shape, indicating that little kinetic energy is released. In the case of compound **1b** (R = OCH_3), $\epsilon_r^\ddagger$ increases by 0.2 eV, but the relevant signal is only slightly broadened, remaining Gaussian in shape. Thus, in spite of a substantial increase in $\epsilon_r^\ddagger$, only a minor increase in the kinetic energy release is observed. This is discussed further in the next section.

Further reduction in the dissociation energy of the bond being broken leads to a further increase in $\epsilon_r^\ddagger$. In the case of the endothermic or thermoneutral reactions of **1c**—**1e** (R = CF_3, H, CH_3) this energy is channelled almost completely into the translational energy of the products. The peaks corresponding to loss of substituents from the metastable molecular ions are now strongly broadened and clearly deviate from the Gaussian. This indicates that $\epsilon_r^\ddagger$ now consists mainly of the fixed activation energy for the reverse reaction, ϵ_r^0, and that the non-fixed energy, $\epsilon^\ddagger$, plays only a minor role. In the case of the exothermic reactions of $\mathbf{1f}^{+\cdot}$, $\mathbf{1g}^{+\cdot}$ and $\mathbf{1h}^{+\cdot}$ (R = Cl, Br, NO_2), $\epsilon_r^\ddagger$ increases to 2.2 eV (R = NO_2), with a corresponding increase in

* The fact that ΔH_f = 6.4 eV for the $C_{10}H_9O^+$ ions from *ortho*-fluorobenzalacetone indicates that they are also formed as ions 3^+. The lack of any detectable signal in the MIKE spectrum of ions 3^+ formed from compound **1a** shows that they must be formed without sufficient excitation energy ϵ^* for further decomposition.

ϵ_r^0. Nevertheless, the peaks for the loss of a substituent from the metastable molecular ion are Gaussian-shaped, and the kinetic energy released in no way reflects the large increase in $\epsilon_r^\ddagger$.

The fraction of ϵ_r^0 which appears as translational energy is defined by the energy partitioning ratio q given as $q = T_B/\epsilon_r^\ddagger$ in Table 1. In the case of compound 1a, and probably also 1b, $\epsilon_r^\ddagger$ consists mainly of the freely fluctuating excess energy, ϵ^+, of the activated complex. The partitioning ratios for these reactions must be considered separately, since the partitioning of ϵ^+ is presumably influenced by factors other than those affecting ϵ_r^0 [7f]. For the remaining compounds, however, ϵ^+ can be neglected as discussed above. It appears (Table 1) that the energy-partitioning ratio q has a value of 0.9—1.0 for the endothermic or thermoneutral reactions of $1c^{+\cdot}$—$1e^{+\cdot}$, with an abrupt change to q = 0.2—0.3 on going to the exothermic reactions of $1f^{+\cdot}$—$1h^{+\cdot}$.

DISCUSSION

The intramolecular aromatic substitution of the R groups in the molecular ions of *ortho*-substituted benzalacetones $1^{+\cdot}$ requires a small activation energy, $\epsilon_h^\ddagger$ = 0.5—0.6 eV, in all cases except 1h (R = NO_2, see below). This result is remarkable in a number of respects:

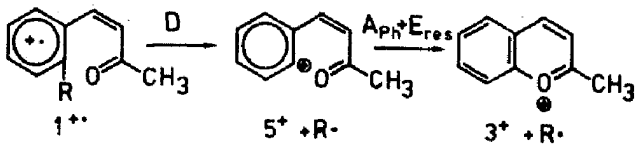
(i) The small value of $\epsilon_h^\ddagger$ proves that the loss of the substituent R from $1^{+\cdot}$ must occur during or following the formation of a new bond. The energy gained thus reduces the activation energy required to break the bond without assistance. Studies on the metastable characteristics of the $C_{10}H_9O^+$ ion [1] have shown that the product ions of reaction 1 are 2-methylbenzopyrylium ions, 3^+; the substituent R is displaced by the oxygen atom of the carbonyl group of $1^{+\cdot}$.

(ii) According to the Bell—Evans—Polanyi (BEP) principle [13], it would be expected that the activation energy would increase with increasing bond dissociation energy, provided that the loss of the substituent is a direct, synchronous displacement reaction. The constancy of the activation energies, $\epsilon_h^\ddagger$, therefore points to a stepwise substitution reaction, with an energy-determining first step which is influenced only slightly by the nature of the substituent. This reaction step could correspond to the formation of an intermediate, $2^{+\cdot}$ (see reaction 1, and below for further discussion) *.

(iii) The linear dependence of the apparent heats of formation, $\Delta H_f'(3^+)$, on the dissociation energies of the bonds to be broken (see Fig. 2) is a consequence of the constant activation energy, $\epsilon_h^\ddagger$. This follows from eqn. (1), and an evaluation of the dependence of the dissociation energy D on the

* It is possible, however, especially in view of the small value of $\epsilon_h^\ddagger$, that the *trans*—*cis* isomerization of $1^{+\cdot}$ constitutes the energy-determining step.

heat of reaction, ΔH^{+}_{R}, is carried out with the aid of the hypothetical reaction 3.



Reaction 3

Equation (4) follows from reaction 3, A_{Ph} being the phenyl ion affinity of the carbonyl group and E_{res} the resonance energy of a pyrylium ion *.

$$\Delta H^{+}_{R} = D - (A_{Ph} + E_{res}) \quad (4)$$

Equation (5) can be obtained from eqns. (2), (3) and (4). A linear increase of $\Delta H^{+}_{f}(3^{+})$ with decreasing D is therefore expected if $\epsilon^{\ddagger}_{h}$ is constant.

$$\Delta H^{+}_{f}(3^{+}) = \Delta H_{f}(3^{+}) + \epsilon_{h} + A_{Ph} + E_{res} - D$$

$$= \text{Constant} - D \quad (5)$$

This has actually been shown to be the case (see Fig. 2) **.

(iv) One of the most remarkable aspects of the constant activation energy $\epsilon^{\ddagger}_{h}$ is the large variation in the intensities of the peaks associated with the formation of ions 3^{+}, m/z 145, in the 70-eV mass spectra of the benzalacetones studied. It has been pointed out previously [1] that the tendency for ions 3^{+} to form increases strongly with decreasing bond dissociation energy, at the expense of the competing fragmentation pathways. The molecular ions of the benzalacetones, $1^{+\cdot}$, react via two main pathways:

(a) formation of 3^{+} by loss of H· or R· radicals from the *ortho* position of the phenyl ring, further decomposition of 3^{+} being negligible,

(b) loss of the terminal CH_3 group and further decomposition of the M — $CH_3]^{+}$ ions.

The mass spectra of compounds 1a, 1c and 1d are dominated by the products of pathway b. In the case of deuterated 1e, loss of the *ortho* and

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* If A_{Ph} is approximated by the methyl cation affinity of formaldehyde, A_{Me} = —3.5 eV (see equation below) and $D(1d^{+\cdot})$ by $D(C_6H_5 - H]^{+\cdot})$ = 3.96 eV (from known values with $\Delta H_f(C_6H_5^{+})$ = 11.8 eV [14]), and taking $\Delta H_f(3^{+})$ = 6.4 eV, an estimate of the hitherto unknown resonance energy of a pyrylium ion, $E_{res} \approx$ 0.3 eV, can be obtained.

CH_3^{+} + $O{=}CH_2$ → $CH_3{-}O^{+}{=}CH_2$ — A_{Me}

11.36 [14] —1.20 [15] 6.63 [16] —3.5 eV

** The agreement also obtained for compound 1h (R = NO_2) may be fortuitous, as the D value of this compound was calculated from I (*p*-nitrobenzalacetone) (see footnote c, Table 1 and the rest of the discussion).

terminal methyl groups occurs to almost the same extent, while for **1b**, **1f**, **1g** and **1h** the abundance of ions 3^+ substantially exceeds that of $M - CH_3^{\bullet}]^+$. Ionized **1a** (R = F) loses hydrogen atoms more easily than fluorine atoms, consistent with the hypothesis outlined above. Compound **1b**, however, constitutes an exception, because, in spite of the high bond-dissociation energy, displacement of the OCH_3 group leads to the base peak in the 70-eV mass spectrum of this compound (see below). The intensity variations described above are only influenced to a very small extent by differences in the appearance energies of the $M - CH_3^{\bullet}]^+$ ions [12]. To illustrate this, Table 2 shows the abundance ratios of the ions 3^+ and $M - CH_3^{\bullet}]^{+\bullet}$ derived from compounds **1a**—**1h** at two different reduced values for the electron energy. This diminishes the influence of any further decomposition of the $M - CH_3^{\bullet}]^{+\bullet}$ ions on the abundance of the non-decomposing $M - CH_3^{\bullet}]^+$ ions.

The tendency towards increasing abundance of 3^+ relative to $M - CH_3^{\bullet}]^+$ with decreasing dissociation energy D is obvious, except in the case of the methoxy compound **1b**. There is also a distinct change in the intensity ratios, from small to much larger values, on passing from compound **1e** (R = CH_3) to **1f** (R = Cl). This is especially noticeable at 15 eV. These differences reflect changes in the rate of formation of 3^+. Since the activation energies for the formation of ions 3^+ do not alter, the changes in the rate of formation must be associated with the details of the reaction path along the reaction coordinate.

A first approach to the type of transition state involved in the formation of ions 3^+ can be made by applying the Hammond principle [17]. According to this principle, the transition state of an exothermic elementary reaction resembles the configuration of the reactants (educt-like transition state),

TABLE 2

Intensity ratio $I\ (3^+)/I\ (M - CH_3^{\bullet}]^+)$ in the mass spectra of **1a**—**1h** at low electron energy

R	E (eV)	
	30	15
F	0.09	0.12
OCH_3	2.1	3.4
CF_3	1.1	1.8
H [a]	0.24	0.42
CH_3	1.1	1.2
Cl [b]	2.8	5.0
Br [b]	4.1	7.2
NO_2	14.1	24.3

[a] Multiplied by symmetry factor 0.5.
[b] Sum of the isotope peaks for $I\ (M - CH_3^{\bullet}]^+)$.

while that of an endothermic reaction resembles the configuration of the products (product-like transition state). For the reaction studied, it has been established that the displacements of the substituents F, OCH_3, H, CF_3 and CH_3 are endothermic or nearly thermoneutral, while those of Cl, Br and NO_2 are exothermic. Intramolecular aromatic substitution therefore involves a product-like transition state in the case of the molecular ions $\mathbf{1a}^{+\cdot}$—$\mathbf{1e}^{+\cdot}$ ("strongly" bound substituents) and a reactant-like transition state for the molecular ions $\mathbf{1f}^{+\cdot}$—$\mathbf{1h}^{+\cdot}$ ("loosely" bound substituents). The division of this displacement reaction into two classes seems to be valid, despite the uncertainties associated with the determination of $\Delta H_f(\mathbf{3}^+)$ and hence ΔH_R^+.

In recent publications Miller [18] and Agmon [9] have independently derived a function ψ which generalizes and quantifies the Hammond postulate. ψ describes the position of the potential energy barrier of an elementary reaction on the reaction coordinate, X_0^*, with respect to the barrier height U^* (here: $\epsilon_h^\ddagger$) and the potential energy of reaction U_f (here: ΔH_R^+) (eqn. 6).

$$X_0^* = \frac{1}{2 - U_f/U^*} = \frac{1}{2 - \Delta H_R^+/\epsilon_h^\ddagger} \tag{6}$$

X_0^* is the value of the reaction coordinate X ($0 \leqslant X \leqslant 1$) corresponding to the position of the activated complex; the positions $X = 0$ and $X = 1$ represent the initial and final states of the reaction, respectively. Figure 3 shows the dependence of X_0^* on U_f calculated with $U^* = 0.45$, 0.55 and 0.65 eV, and the points calculated using the experimentally determined values for $\epsilon_h^\ddagger$ and ΔH_R^+.

The experimental points are in very good agreement with the curve calculated for $U^* = 0.55$ eV in all cases, except for the *o*-nitro compound. The ionization energy of this compound could not be determined because of the very low intensity of the molecular ion. The ionization energy was therefore approximated by using the value of the *para*-nitro isomer, $I = 9.2$ eV, yielding $\epsilon_h^\ddagger = 0.2$ eV. It is possible, however, that *ortho*-interaction of the NO_2 group with the side-chain reduces the π-electron interaction, thus lowering the ionization energy of the *ortho*-nitro compound relative to that of the *para* isomer. This would lead to a higher activation energy $\epsilon_h^\ddagger$ and hence to a smaller deviation from the experimental value for **1h** in Fig. 3.

According to eqn. (6) and Fig. 3 the potential energy barrier varies continuously with the heat of reaction. This corresponds to a significant change in the transition state configurations of the reacting molecular ions of the benzalacetones studied. This tendency is reflected by a parallel change in the abundance of ions $\mathbf{3}^+$; this is large for compounds **1f**—**1h** (R = Cl, Br, NO_2; $X_0^* < 0.5$) and significantly lower in the case of compounds **1a** and **1c**—**1e** (R = F, CF_3, H, CH_3; $X_0^* \geqslant 0.5$). This result shows that the intensities of fragment-ion peaks within a series of analogous mass-spectrometric fragmentations do not depend only on the potential energies of the activated com-

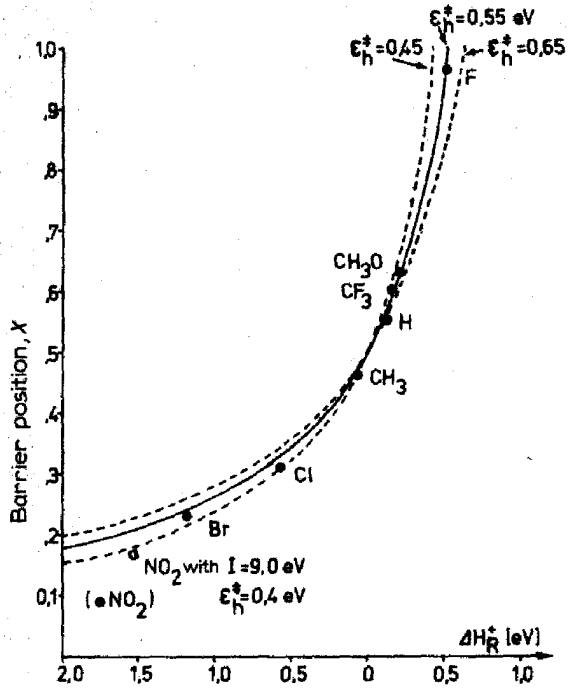

Fig. 3. Correlation between barrier position and heat of reaction for the reaction $1^{+\cdot} \rightarrow 3^{+} + R$; dashed and full lines were calculated for $\epsilon_h^{\ddagger} = 0.55 \pm 0.1$ eV; experimental values as indicated.

plexes, but also on their positions on the reaction coordinate, given by X_0^*.

Following the discussion of the constant activation energy $\epsilon_h^{\ddagger}$ and its various implications, the energy partitioning ratios associated with the formation of ions 3^{+} from *ortho*-substituted benzalacetones (see Table 1) are now discussed in detail. The kinetic energy release related to the reactions of metastable ions has been studied in a variety of single reactions [7]. Most of these investigations are concerned with rearrangement reactions eliminating neutral molecules because a large activation energy for the reverse reaction, $\epsilon_r^{\ddagger}$, is to be expected in these cases. As shown above (see Fig. 2), a large variation in $\epsilon_r^{\ddagger}$ can also be achieved by systematically varying the substituent to be displaced in a substitution reaction. The principal factors underlying the energy partitioning of an activated complex can therefore be studied in relation to the thermochemistry of the reaction, and then by applying the Hammond postulate [9,17,18] to the configuration of the activated complex.

The factors which determine the fraction of energy in the transition state to be released as kinetic or rotational energy and that which remains as internal energy of the products have not yet been thoroughly investigated. Some authors claim that orbital-symmetry arguments can be applied to the problem, symmetry-forbidden reactions releasing more kinetic energy than symmetry-allowed reactions [7g,19,20]. Using the reverse argument it has been attempted [20] to correlate a small kinetic energy release with an

orbital-symmetry allowed reaction. Recently, however, it has been pointed out by Christie, Derrick and Rickard that this argumentum e contrario may be invalid [21], as the amount of kinetic energy released may be governed by factors quite different from those affecting the conservation of orbital symmetry. Furthermore, the approach of Christie et al. to the problem is more general, as they take into account the detailed motion of the reacting atoms on the potential-energy surface, thus relating the problem of energy partitioning with the geometry of the transition state. This approach has previously been taken by several other authors [7a,22,23] but no systematic study has yet been reported. The reaction investigated in this work makes it possible to discuss the energy-partitioning in relation to the position of the activated complex on the reaction coordinate, X_0^*.

It has been shown (Table 1, and previous discussion) that the energy-partitioning ratio, $q = T_B/\epsilon_r^\ddagger$, can be used to divide the intramolecular aromatic substitution of *ortho*-substituted, ionized benzalacetones into two classes, one with $q = 1.0$—0.9 (R = F, CF_3, H, CH_3) and the other with $q = 0.2$—0.3 (R = Cl, Br, NO_2). It is perhaps surprising to note that this classification corresponds to a division established previously in connection with the abundance of ions 3^+ produced by the benzalacetones studied. A connection must therefore exist between the position of the energy barrier on the reaction coordinate, X_0^*, and the energy-partitioning ratio q, such that q is large for $X_0^* \gtrsim 0.5$ (endothermic/thermoneutral reactions) and that q is small for $X_0^* < 0.5$ (exothermic reactions).

The methoxy-substituted benzalacetone **1b** constitutes an exception in both cases: the abundance of ions 3^+ is too high and the energy-partitioning ratio is too low.

It is possible, however, that an isomeric neutral (the CH_2OH radical) may be formed during the reaction, thus influencing the thermochemistry of elimination. If $\Delta H_f(HOCH_2^+) = -0.20$ eV, the heat of reaction becomes $\Delta H_R^+ = -0.14$ eV so that the reaction changes from being endothermic (loss of $^\cdot OCH_3$) to exothermic (loss of $HOCH_2^+$). There is then a corresponding change in intensity and energy partitioning.

The effect of the position of the energy barrier on the reaction coordinate of simple exchange reactions has been studied theoretically by Polanyi et al. [8,24,25]. It was shown that, in the case of product-like transition states (repulsive or late-downhill surface), a large amount of the available energy is channelled into translation of the separating products. In the case of an educt-like transition state (attractive or early-downhill surface), however, most of the energy of the activated complex remains in the products as internal excitation energy. Intramolecular substitution of the ionized benzalacetones **1a** and **1c**—**1e** generates ions 3^+ via a product-like transition state, characterized by $X_0 \gtrsim 0.5$. Nearly all of the available energy, $\epsilon_r^\ddagger$, is found as kinetic energy, T_B, in these compounds. In the case of the benzalacetones **1f**—**1h** (and possibly **1b**) the transition state is educt-like, $X_0 < 0.5$, and only a minor part of the transition state energy is found as kinetic energy, T_B; the

complementary amount of energy must therefore remain in the products, mainly as excitation of ions 3^+. It therefore appears likely that the theoretical concepts concerning energy partitioning [8] are valid not only for three-atomic systems but also in principle for "big" molecules or ions. Mass-spectrometric methods seem well suited to test such concepts experimentally in many-atom systems.

A correlation between the energy-partitioning ratio q and X_0^* makes it possible to obtain experimental information about the nature of the transition state produced in a mass-spectrometric fragmentation reaction, and thus provides more detailed data on these elementary reactions. The formation of ions 3^+ from $\mathbf{1a}^{+\cdot}$, $\mathbf{1c}^{+\cdot}$, $\mathbf{1d}^{+\cdot}$ and $\mathbf{1e}^{+\cdot}$ takes place with the transformation of nearly all the available energy into translational energy, measured as the maximum kinetic energy release, T_B. In the case of the strongly endothermic reaction of $\mathbf{1a}^{+\cdot}$ ($X_0^* = 0.95$) this amount of energy is small, as the available energy of the product-like transition state corresponds only to the excess energy $\epsilon^{\ddagger}$ *. The energy available and T_B increase considerably, however, in the case of the weakly endothermic or thermoneutral reactions of $\mathbf{1c}^{+\cdot}$, $\mathbf{1d}^{+\cdot}$ ($X_0^* = 0.60$) and $\mathbf{1e}^{+\cdot}$ ($X_0^* = 0.46$), without a noticeable change in q. However, T_B decreases sharply in the clearly exothermic reaction of $\mathbf{1f}^{+\cdot}$ ($X_0^* = 0.31$), in spite of an increase in the energy $\epsilon_r^{\ddagger}$ available; the major part of $\epsilon_r^{\ddagger}$ appears as internal energy of the products and q decreases to small values. The structure of the potential-energy surface in the vicinity of the reaction coordinate for these reactions obviously does not allow a strong coupling of the motion along the reaction coordinate with other degrees of freedom when $X_0^* > 0.4$. The reaction coordinate for $X_0^* > 0.4$ can therefore be regarded as a stretching of the bond between the substituent and the rest of the molecule — possibly as part of an intermediate $\mathbf{2}^{+\cdot}$ (see reaction 1), which is flattened to the aromatic system of the benzopyrylium ion 3^+. At values $X_0 < 0.4$, however, realized in compounds **1f**—**1h** which have loosely-bound substituents, the major part of $\epsilon_r^{\ddagger}$ flows into degrees of freedom other than translation. In these cases the reaction coordinate must correspond to a complicated coupled motion of several atoms or groups of atoms in the activated complex. The educt-like transition states therefore resemble the intermediate $\mathbf{2}^{+\cdot}$, whose geometry is quite different from the planar structure of the benzopyrylium ion 3^+, thus leading to vibrationally excited 3^+.

The fact that nearly all the available energy $\epsilon_r^{\ddagger}$ is channelled into translation for elimination of F, CF_3, H and CH_3 from $\mathbf{1a}^{+\cdot}$ and $\mathbf{1c}^{+\cdot}$—$\mathbf{1e}^{+\cdot}$ is probably an artifact of the system studied, in that the connection between the position of the activated complex and translational energy released is especially clear. In general, it will probably be found that a large proportion of the energy available, $\epsilon_r^{\ddagger}$, will appear as translational energy, but the special case $q = 1$ will be observed only if the reaction progresses smoothly along the reaction coordinate. Therefore it seems more important to detect a change in

* See also footnote on page 277.

q, which occurs when the reaction switches from an early to a late transition state. This should also be observed with other mass-spectrometric fragmentation reactions.

EXPERIMENTAL

The 70-eV mass spectra, the ionization and appearance energies and the translational energies were determined as described elsewhere [1]. The reproducibility of the ionization and appearance energies is better than ±0.1 eV and ±0.2 eV, respectively, and within a typical range of ±0.05 eV and ±0.1 eV. The maximum value of the kinetic energies, T_B, were determined from the base-widths of the peaks in the MIKE spectra; the reproducibility is ±5% of the absolute values in most cases. The peak for elimination of hydrogen from metastable $1d^{+\cdot}$ is unsymmetric due to the neighbouring peak derived from stable $1d^{+\cdot}$, and was corrected correspondingly; the peak for NO_2-elimination from metastable $1h^{+\cdot}$ is noisy due to low intensity. In both cases the reproducibility is within ±10% of the absolute values.

Thermochemical data were determined from the literature [14,15,26] or by incremental methods [27]. The agreement between experimental ΔH_f values and those derived from increments is within ±0.1 eV.

All compounds **1a**—**1h** are known, except **1c**.

3-Butene-2-one-4-(2-trifluoromethylphenyl), 1c

8.7 g (0.05 mole) of 2-trifluoromethylbenzaldehyde, **6**, are shaken together with a mixture of 13 g acetone (0.22 mole), 60 ml of water and 5 ml of a 10% aqueous NaOH solution under nitrogen on a shaking machine. After a period of 2 h, **6** is no longer detected (TLC). Following neutralization with dilute acetic acid and work-up, the crude product is vacuum distilled; b.p. (0.3 torr): 98—101°C; yield: 6.0 g ~ 56%. Part of this fraction is further purified by column-chromatography (silica-gel, 30—70 mesh; eluant: benzene/ethyl acetate 10 : 1).

Elementary analysis: $C_{11}H_9F_3O$ (m.w. 214.2); exp. (calc.): C 60.16 (61.68); H 4.24 (4.25).

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