418. *Arrhenius Parameters of Some Reactions involving Multiplicity Changes.*

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Arrhenius parameters have been determined for the thermal decomposition in the presence of toluene of hexafluoroazomethane, acetone, trifluoroacetone, acetophenone, trifluoroacetophenone, benzophenone, and dibenzyl ketone; high frequency factors were observed for compounds containing aryl groups. A possible explanation of this phenomenon is suggested.

In compounds of the type R_2X where the R–X bond is relatively weak, there are two possible free-radical decomposition mechanisms or modes. These are

$$R_2X \longrightarrow RX\cdot + R\cdot \quad . . . . \quad (1a)$$

followed by

$$RX\cdot \longrightarrow R\cdot + X \quad . . . . \quad (1b)$$

or alternatively

$$R_2X \longrightarrow R\cdot + R\cdot + X \quad . . . . \quad (2)$$

The second possibility is important as the activation energy of process (1*b*) is generally small, because during this dissociation the system X can revert from its bivalent to its zero-valent state; hence, decompositions by either mechanism will differ little in activation energy and, if their frequency factors differ suitably, they may even occur simultaneously in the experimental temperature range. In general, reaction (2) will have a high frequency factor offsetting to some extent its higher activation energy, and the high frequency factors which occur in the thermal decomposition of the mercury alkyls have been explained in terms of the simultaneous occurrence of both modes of decomposition.[1] We now present

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[1] Pritchard, *J. Chem. Phys.*, 1956, in the press.

results for a series of other molecules, all showing this feature of a multiplicity change during the reaction which renders their thermochemistry qualitatively similar to that of the alkylmercury molecules; their behaviour is also similar, the decompositions having a normal frequency factor (10^{13}—10^{14} sec.$^{-1}$) when R is small, but a much larger one (10^{15}—10^{17} sec.$^{-1}$) when R is a large group.

EXPERIMENTAL

Materials.—Sulphur-free toluene was twice pyrolysed at about 840° and then fractionated over phosphoric oxide. The main fraction boiling over a range of 0·04° was degassed by repeated bulb-to-bulb distillation *in vacuo* before use. Hexafluoroazomethane was prepared by heating equal quantities of iodine cyanide and iodine pentafluoride; details are given elsewhere.[2] Trifluoroacetophenone, prepared by the reaction of trifluoroacetyl chloride with benzene in carbon disulphide at 5°, aluminium trichloride being used as catalyst,[3] had b. p. 85·6°/32 mm. [2 : 4-dinitrophenylhydrazone, m. p. 92·0—92·5° (Found : F, 32·5. Calc. for $C_8H_5OF_3$: F, 32·8%)]. Trifluoroacetone, obtained from Caribou Chemical Co. (Columbus, Ohio), was dried, distilled, and degassed before use. Acetone (" AnalaR ") was fractionated over anhydrous magnesium sulphate and degassed before use. Commercial acetophenone was distilled and repeatedly fractionally frozen. Commercial benzophenone, m. p. 48·0° (sharp), was used. Dibenzyl ketone, supplied commercially as a brown liquid, was fractionally frozen and crystallised from light petroleum; the product (colourless needles, m. p. 34·0°) was stored in the dark.

Apparatus and Procedure.—The toluene carrier technique has been described, together with the modifications for gases or involatile solids;[4] our procedure followed these except for the use of quartz capillaries instead of quartz wool as a test for heterogeneity.[5] A toluene pressure of 13 ± 1 mm. was used and the reactant pressure kept at about 1% of this value once the first-order nature of the decomposition had been demonstrated. The extent of reaction was determined from the amount of nitrogen or carbon monoxide collected. In the case of hexafluoroazomethane, nitrogen was the only non-condensable gas produced, but at the high temperatures needed with the ketones small quantities of methane and hydrogen were produced from the toluene; the amount of carbon monoxide formed was therefore determined by oxidation with iodine pentoxide at 125°, which does not affect hydrogen or methane. For trifluoromethyl compounds the percentage decomposition was checked by measuring the amount of fluoroform produced.

DISCUSSION

The results are shown in the Figure, and the Arrhenius parameters determined from them by the method of least squares are listed in Table 1; the molecules studied behave like mercury dialkyl analogues in that high frequency factors occur when large groups present. Further discussion is restricted by lack of reliable thermochemical data; the are following heats of formation of radicals (ΔH_f) are accepted in this paper : $CH_3\cdot$, 32·6; $C_6H_5\cdot$, 69; $C_6H_5\cdot CH_2\cdot$, 37·5; $CH_3\cdot CO\cdot$, −11·8; $C_6H_5\cdot CO\cdot$, 15·6 kcal./mole. The only

TABLE 1.

Compound	Activation energy (kcal./mole)	Frequency factor (sec.$^{-1}$)	Compound	Activation energy (kcal./mole)	Frequency factor (sec.$^{-1}$)
Azomethane [a]	46·0	$1·5 \times 10^{14}$	Acetophenone	77·6	$5·1 \times 10^{15}$
Hexafluoroazomethane ...	48·5	$9·0 \times 10^{13}$	Trifluoroacetophenone ...	73·8	$1·8 \times 10^{15}$
Acetone [b]	70·9	$1·4 \times 10^{14}$	Benzophenone	87·5	$1·6 \times 10^{16}$
Trifluoroacetone	67·8	$3·0 \times 10^{13}$	Dibenzyl ketone	71·8	$1·8 \times 10^{17}$

(*a*) Data from Page, Pritchard, and Trotman-Dickenson.[6] (*b*) Professor M. Szwarc (personal communication) reports $E = 72$ kcal./mole, $A = 2·4 \times 10^{14}$ sec.$^{-1}$.

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[2] Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, in the press.

[3] Simons and Ramler, *J. Amer. Chem. Soc.*, 1943, **65**, 389.

[4] Sehon and Szwarc, *Proc. Roy. Soc.*, 1950, *A*, **202**, 263; Szwarc, Ghosh, and Sehon, *J. Chem. Phys.*, 1950, **18**, 1142; Leigh, Sehon, and Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 91.

[5] Clark, Pritchard, and Trotman-Dickenson, *J.*, 1954, 2633.

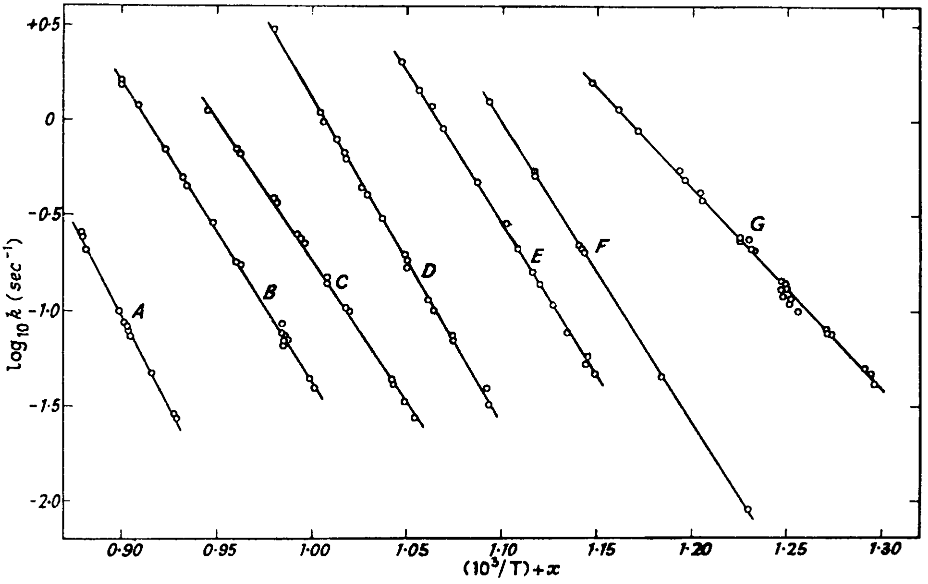
[6] Page, Pritchard, and Trotman-Dickenson, *J.*, 1953, 3878.

figure needing comment is that for the phenyl radical which Pritchard[1] took as 74·8 kcal./mole, this being the only literature value which does not require the critical energy of activation (ε*) for diphenylmercury to exceed the heat of the reaction; however, as this work has revealed some reactions where this obviously is the case, we now adopt a more generally accepted value for the C–H dissociation energy in benzene.[7]

Despite the limitation in thermochemical data, several interesting features of reactions involving multiplicity changes emerge.

1. *Effect of Fluorine Substitution.*—Our results show that the replacement of CH_3 by CF_3 has very little effect on either the activation energy or the frequency factor. The latter observation does not support the contention that the effective number of oscillators (*s*) contributing to the reaction should increase with the physical mass of the end groups;[1] thus the value of *s* is determined predominantly by the complexity of the end groups.

Arrhenius plots of some reactions involving multiplicity changes.



A, Benzophenone ($x = 0$); B, acetone ($x = 0$); C, trifluoroacetone ($x = +0·04$); D, acetophenone ($x = +0·08$); E, trifluoroacetophenone ($x = +0·12$); F, dibenzyl ketone ($x = 0$); G, hexafluoroazomethane ($x = -0·15$).

2. *Reactions in which* ε* *is greater than* Δ*H*.—For azomethane,[6] the sum $(D_1 + D_2)$ of the two C–N dissociation energies has been estimated at about 22 kcal., compared with the observed value of $E = 46$ kcal.; hexafluoroazomethane is presumably a similar case. This phenomenon is most marked in the decomposition of dibenzyl ketone. From combustion measurements [8] ΔH_f for gaseous dibenzyl ketone is 1·0 kcal./mole, whence $(D_1 + D_2) =$ 47·6 kcal. This is very substantially less than the observed activation energy of 72 kcal., and the occurrence of an extremely high *A*-factor suggests that ε* is significantly greater than 72 kcal. (cf. ref. 1). Benzyl methyl ketone is similar: using $\Delta H_f = 22·6$,[9] we find $(D_1 + D_2) = 66·3$ kcal., whereas the observed rate constant of decomposition [10] is $k = 9 \times 10^{15} \exp(-68·2/\mathbf{R}T)$ sec.⁻¹. Thus the observed *E* is probably a little larger than $(D_1 + D_2)$ and, in view of the high frequency factor, ε* is substantially greater than $(D_1 + D_2)$. It appears that this is not an isolated phenomenon and we are now inclined to add diphenylmercury to the list of cases of its occurrence; it was shown [1] that ε* has

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[7] Chernick, Skinner, and Wädso, *Trans. Faraday Soc.*, 1956, in the press.
[8] Springall and White, *J.*, 1954, 2764; White, Ph.D. Thesis, Manchester, 1951.
[9] Nicholson, Szwarc, and Taylor, *J.*, 1954, 2767.
[10] Taylor, Ph.D. Thesis, Manchester, 1953.

to be of the order of 74 kcal. in order to explain the observed values of E (68·0 kcal.) and A (1×10^{16} sec.$^{-1}$) whereas $(D_1 + D_2)$ is probably not greater than 62 kcal./mole. We know of no convincing explanation why these molecules should behave differently from their homologues.

3. *Compounds containing One Carbonyl Group.*—Of the three remaining ketones in Table 1 (acetone, acetophenone, and benzophenone), only acetone shows what may be regarded as a " normal " frequency factor, suggesting that its decomposition proceeds mainly by mode 1, *i.e.*, fission into two fragments. This interpretation is borne out by the thermochemistry of the reactions, since $(D_1 + D_2) = 90{\cdot}6$ kcal. whereas $D_1 = 72{\cdot}6$ kcal., which is very close to the observed activation energy of 71 kcal./mole. In the other two cases, the frequency factor is definitely high and a reasonable description of both reactions can be given in terms of decomposition by mode 2, *i.e.*, fission into three fragments.

It is clear that we need not adhere to the concept of strict localisation of critical energy within the bonds being broken. In the course of the reaction, the C–O bond length changes from 1·20 to 1·13 Å and it follows that the concentration of energy in any vibration which seriously affects the length of the C–O bond will reduce the energy required to rupture the two C–C bonds. The effect of this is to increase the effective number (s) of oscillators that we may consider as contributing to the decomposition. For these two ketones we have the following thermochemical data (kcal./mole) : [8, 11]

	ΔH_f (s)	$\lambda_{\text{vap.}}$	ΔH_f (g)	$\varepsilon_1^* = D_1$	$\varepsilon_2^* = (D_1 + D_2)$
Acetophenone	−36·8	16·7	−20·1	68·3	96·0
Benzophenone	−7·9	20·4	14·2	72·8	100·5

In each case, mode 1 ($s = 1$), and mode 2 ($s = 6$) give rate constants calculated from

$$k = \lambda\left[\exp\left(-\frac{\varepsilon^*}{kT}\right)\right]\sum_{r=0}^{s-1}\left[\frac{1}{r!}\left(\frac{\varepsilon^*}{kT}\right)^r\right]$$

of the same order of magnitude as those observed, by using $\lambda = 2{\cdot}5 \times 10^{12}$ sec.$^{-1}$ and T corresponding to the middle of the experimental temperature range. Calculation of the theoretical rates with these values of s for other temperatures (cf. ref. 1) leads to $k = 5{\cdot}0 \times 10^{15} \exp(-81{\cdot}3/\boldsymbol{R}T)$ for acetophenone and $k = 1{\cdot}5 \times 10^{16} \exp(-87{\cdot}5/\boldsymbol{R}T)$ for benzophenone; these are very similar to the observed parameters in Table 1.

4. *Compounds containing Two Carbonyl Groups.*—Three such compounds have been studied kinetically; these are diacetyl,[10] benzil,[12] and di-*tert.*-butyl peroxide.[13] Fission into two, three, and four fragments has to be considered: for the first two compounds sufficient thermochemical data are available to treat the three modes

$$\text{R·CO·CO·R} \longrightarrow \text{R·CO·} + \text{·COR (mode 1)}, \varepsilon_1^*$$

$$\text{R·CO·CO·R} \longrightarrow \text{R·} + \text{CO} + \text{·COR (mode 2)}, \varepsilon_2^*$$

$$\text{R·CO·CO·R} \longrightarrow \text{R·} + \text{CO} + \text{CO} + \text{R· (mode 3)}, \varepsilon_3^*$$

We have no data for a fourth mode, R·CO·CO·R ⟶ R· + ·CO·CO·R, but we consider it an unlikely possibility and will ignore it. Also, for the peroxide, only the three reasonable modes

$$\text{Me}_3\text{C·O·O·CMe}_3 \longrightarrow \text{Me}_3\text{CO·} + \text{·O·CMe}_3 \text{ (mode 1)}, \varepsilon_1^*$$

$$\text{Me}_3\text{C·O·O·CMe}_3 \longrightarrow \text{Me·} + \text{Me}_2\text{CO}.+ \text{·O·CMe}_3 \text{ (mode 2)}, \varepsilon_2^*$$

$$\text{Me}_3\text{C·O·O·CMe}_3 \longrightarrow \text{Me·} + \text{Me}_2\text{CO} + \text{Me}_2\text{CO} + \text{Me· (mode 3)}, \varepsilon_3^*$$

are considered; for the critical energy for mode 1, we have taken the observed O–O bond dissociation energy [14] for diethyl peroxide of 31·7 kcal., because the activation energy

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[11] Parks, Mosley, and Peterson, *J. Chem. Phys.*, 1950, **18**, 152.
[12] Jacquiss, Ph.D. Thesis, Manchester, 1953.
[13] Pritchard, Pritchard, and Trotman-Dickenson, *J.*, 1954, 1425.
[14] Rebbert and Laidler, *J. Chem. Phys.*, 1952, **20**, 574.

observed for di-*tert.*-butyl peroxide obviously cannot be identified with a simple bond-breaking process in view of the enormous frequency factor with which it is associated. Thus, we have [9, 8, 15]

	ΔH_f (*g*)	ε_1^*	ε_2^*	ε_3^*	
Diacetyl	−78·1	54·5	72·5	90·5	kcal./mole.
Benzil	−21·8	53·0	80·7	108·4	kcal./mole.
Di-*tert.*-butyl peroxide	−26·5	31·7	39·0	46·3	kcal./mole.

By using these parameters as before [1] and taking $\lambda = 10^{12}$ sec.$^{-1}$ the results in Table 2 were obtained; the agreement between experimental and calculated Arrhenius parameters is most encouraging.

TABLE 2.

	Observed Arrhenius parameters		No. of oscillators assumed			Calculated Arrhenius parameters	
Molecule	*A* (sec.$^{-1}$)	*E* (kcal.)	Mode 1	Mode 2	Mode 3	*A* (sec.$^{-1}$)	*E* (kcal.)
Diacetyl	5·2 × 10^{15}	66·0	1	4	9	4·5 × 10^{15}	67·2
Benzil	2·0 × 10^{16}	66·4	1	6	12	1·6 × 10^{16}	67·5
Di-*tert.*-butyl peroxide ...	4·0 × 10^{16}	39·0	1	4	8	6·6 × 10^{16}	38·8

The calculations described in **3** and **4** above contain in effect only one arbitrary parameter, *i.e.*, the value of λ assumed. A value for λ having once been chosen, the various values of *s* follow automatically, being those which cause their respective modes of decomposition to have calculated rate constants roughly equal to the observed rate constant. We do not know what factors determine the value of λ applicable to any given series of molecules: in the alkylmercury series [1] a value of 1·5 × 10^{13} sec.$^{-1}$ was chosen from a consideration of the molecular vibration frequencies, but in view of the significantly lower values needed for the ketones discussed in this paper it is probable that this choice was fortuitous. However, allowing for an arbitrary choice of λ, one can give a reasonable interpretation of most of the high frequency factors which occur in the alkylmercury and ketone series in terms of the simultaneous decomposition by two or more mechanisms. The only incongruous case is that of benzoyl chloride which decomposes [10] with a " high " frequency factor of 2 × 10^{15} sec.$^{-1}$, but with an activation energy of 74 kcal./mole which corresponds almost exactly to the dissociation energy of the $C_6H_5{\cdot}CO{-}Cl$ bond; in this respect, however, it is interesting that benzoyl bromide also decomposes [16] with an activation energy equal to the $C_6H_5{\cdot}CO{-}Br$ bond dissociation energy, but in this case the frequency factor of 5 × 10^{13} sec.$^{-1}$ is normal.

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[15] Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88.

[16] Ladacki, Leigh, and Szwarc, *Proc. Roy. Soc.*, 1952, *A*, **214**, 273.