The Unimolecular Decompositions of Some Alkyl Bromides

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TABLE I.

	U (kcal/mole)	Lvap (kcal/mole)
Li	9.3±0.35	32.6
Na	9.1±0.1	23
K	9.1±0.1	19.3

Gutowsky is very pleasing, the more so since their results are deduced from a *diffusion-rate* essentially, while ours depend on an equilibrium number of lattice vacancies. The surprising feature, of course, is the remarkable constancy of the activation energy since on the basis of Frenkel or Schottky defects (e.g., Frenkel[2]), one would expect U to depend directly on the latent heat of vaporization which for these three metals is shown in the third column of Table I for comparison. The behavior is perhaps less surprising if one considers the equation $\Delta H = 16.5 L_{\text{melt}}$ proposed recently by Nachtrieb *et al.*[3]

It may be remarked that no exponential resistance rise of this type is observed in Rb and Cs. This would accord with their lower melting points, since it is then unlikely that a sufficient number of vacancies of an activation energy ~9 kcal/g atom could be generated to produce an observable resistance.

[1] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. **20**, 1472 (1952); H. S. Gutowsky, Phys. Rev. **83**, 1073 (1951).
[2] J. F. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), p. 13.
[3] Nachtrieb, Weil, Catalano, and Lawson, J. Chem. Phys. **20**, 1189 (1952).

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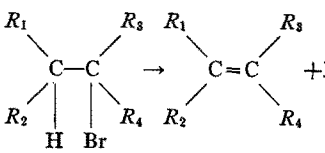
As has been previously reported,[1-3] there is a possible duality of mechanism for the decomposition of alkyl bromides in the gas phase into an olefin and HBr. In the first place, elimination of HBr may proceed in a single step,[3]



(A)

or secondly the initial process may be the breaking of a C—Br bond,[1,2]

$$R\text{—Br} \rightarrow R + \text{Br}. \qquad \text{(B)}$$

In this latter case, the bromine atom may initiate chains, which will lower the over-all activation energy below the value for breaking the C—Br bond and thus enable mechanism (B) to complete favorably with (A). The present note describes some investigations on the unimolecular elimination mechanism which have been obtained by inhibiting the chain mechanism with cyclohexene. This substance was suggested by the work on cyclohexyl bromide (J.H.S.G.), and its enhanced efficiency as compared with propylene has been demonstrated by one of us (P.J.T.).

The parameters of the Arrhenius equations obtained for the maximally inhibited reactions are shown in Table I. All the decompositions when carried out in seasoned vessels are homogeneous and of the first order. Since the chain mechanisms have been eliminated, it may be concluded that they proceed according to mechanism A. Daniels and his co-workers[4] have examined in some detail, the pyrolysis of ethyl bromide and have come to the conclusion that chains certainly play an appreciable part in the noninhibited reaction. This view is confirmed by our study of

TABLE I.

Molecule	log$A$	E (kcal)
ethyl bromide	13.42	53.9
n-propyl bromide	12.90	50.7
n-butyl bromide	13.18	50.9
iso-butyl bromide	13.05	50.4
sec-propyl bromide[a]	13.62	47.8
sec-butyl bromide[a]	12.63	43.8
cyclo-hexyl bromide[a]	13.38	46.1
tert-butyl bromide[a]	14.00	42.2

[a] For these substances no inhibition was observed.

the unimolecular elimination. That a fine state of balance exists between the chain and the unimolecular mechanisms is shown by a comparison of Daniels' value for the parameter of the over-all reaction ($E = 53.0$, log$A = 14.06$) with our own. It should be noted, however, that the addition of cyclohexene in the present experiments did reduce the normal rate and also eliminated the induction periods. A further comparison can be made with the work of Kistiakowsky and Stauffer[5] in the case of *tert*-butyl bromide. These authors rightly concluded that the decomposition proceeded by a unimolecular mechanism, although no attempt was made to inhibit the reaction. Our work has shown that in fact the normal rate is uninfluenced by the addition of an inhibitor. Although our parameters for the reaction differ slightly from those of the earlier workers ($E = 40.5$ kcal, log$A = 13.48$), the disagreement is within the bounds of experimental error. It will also be noted that the limiting rate observed in the case of *n*-propyl bromide is not that of a heterogeneous reaction as suggested previously.[2]

Some tentative conclusions may be drawn from the reported values of the Arrhenius parameters. In the first place, the series further establishes the relationship $A \sim 10^{13}$ for unimolecular reactions. Secondly, in the case of the primary bromides, neglecting ethyl bromide, there is no significant difference in the parameter in going from *n*-propyl to *iso*-butyl bromide. This constancy is further being checked by one of us (J.H.S.G.) in the cases of *n*-pentyl and *n*-hexyl bromide. Again, the decompositions clearly divide themselves as regards activation energy into 3 classes dependent upon the nature of the C—Br bond broken. For primary, secondary, and tertiary bromides the activation energies are of the order of 50, 46, and 42 kcals, respectively. There is thus a clear correlation with C—Br bond strength.

The relationship between the nature of the C—Br and C—H bonds broken is brought out by an examination of the rates relative to the rate of decomposition of ethyl bromide at 380°. Reading across Table II, the enormous effect of varying the C—Br

TABLE II.

p-C—Br		*s*-C—Br		*t*-C—Br	
ethyl	1	*sec*-propyl	170[b]	*t*-butyl	32 000[b]
n-propyl	3.6	*sec*-butyl	390[b]		
n-butyl	5.9	*cyclo*-hexyl	370[b]		
n-pentyl	7.7[a]				
iso-butyl	6.5				

[a] Based on observed rate only.
[b] Obtained by extrapolation.

bond from primary to tertiary is seen, the C—H bond remaining primary. In the first column, the effect of changing the C—H bond from primary to tertiary is seen to be small, as is also the case in column two, where the C—H bond changes from primary to secondary. The conclusion that the C—Br bond strength is the major factor in determining the rate is thus amply justified.

Further details respecting this work will be published elsewhere.

[1] Allan Maccoll, J. Chem. Phys. **17**, 1350 (1949).
[2] P. Agius and Allan Maccoll, J. Chem. Phys. **18**, 158 (1950).
[3] Allan Maccoll and P. J. Thomas, J. Chem. Phys. **19**, 977 (1951).
[4] J. Am. Chem. Soc. **72**, 424 (1950) (reference to earlier work will also be found here).
[5] J. Am. Chem. Soc. **59**, 165 (1937).