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M. Szwarc and A. H. Sehon

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havior. This is done by writing, from Eq. (1):

$$-E^*=c/2r^{*6}$$

where c is the coefficient of the r^{-6} term in the intermolecular potential. For the almost nonpolar molecules considered here only dispersion forces contribute to c. It is convenient to use the derivation of these forces by Slater and Kirkwood and by Kirkwood,⁴ which gives:

$$c = 3eh(N\alpha^3/m)^{\frac{1}{2}}/8\pi\cdots$$
 (2)

in which e and m are the electronic charge and mass, h is Planck's constant, α is the polarizability of the molecule and N is the number of electrons in the molecule. In the present calculations the molecular polarizabilities have been estimated from the refractive indices of the gases and the values l (Table I) have been used for r^* .

The figures for $E^*(calc)$ determined in this way have been plotted against $E^*(exp)$ (from second virial coefficient data references as in Table I) in Fig. 1. The extent of agreement between the experimental and calculated values is remarkable considering that Eq. (2) is only approximately applicable to manyelectron molecules and that E^* is enormously dependent upon the value chosen for r^* . The outstanding failures of the theory occur for the linear triatomic molecules N₂O and CO₂ and may be due to the rather wide departure of these molecules from spherical symmetry.

¹ Bird, Spotz, and Hirschfelder, J. Chem Phys 18, 1395 (1950), ² Hirschfelder, McClure, Curtiss, and Osborne, N.D.R.C. Rep. A116

⁴ Hirschleider, McCenter, Carson, J. (1942).
³ L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1940), p. 189
⁴ J C. Slater and J. G. Kirkwood Phys. Rev. 37, 682 (1931) J. G Kirkwood, Physik. Z. 33, 57 (1932).

The Effect of Halogenation on the C-Br Bond **Dissociation Energy in Halogenated** Bromomethanes

M. SZWARC AND A H SEHON Chemistry Department, University of Manchester, Manchester, England (Received March 13, 1951)

THE pyrolyses of methyl bromide and of the halogenated bromomethanes: CH2ClBr, CH2Br2, CHCl2Br, CHBr3, CF3Br, CCl3Br, and CBr4 were investigated by the use of the "toluene carrier" technique. It was shown that all these decompositions were initiated by the unimolecular dissociation process

$$R.Br \rightarrow R \cdot + Br. \tag{1}$$

Since these reactions were carried out in the presence of an excess of toluene, the bromine atoms produced in process (1) were removed by the fast reaction (2)

$$C_{6}H_{5}.CH_{3}+Br\rightarrow C_{6}H_{5}CH_{2}\cdot+HBr.$$
(2)

Hence, the rate of the unimolecular dissociation process (1) was measured by the rate of formation of HBr. Furthermore, the formation of dibenzyl in the pyrolysis of each of these bromomethanes revealed clearly the radical mechanism of the over-all decomposition.

The kinetics of these pyrolyses showed that the investigated processes were essentially homogeneous gas reactions of the first order with respect to the bromide The rate constants were affected, however (except in the case of CCl₃Br and CBr₄), by the pressure of toluene. The dependence of the rate of decomposition on the toluene pressure forced us to abandon the calculation of activation energies from the temperature coefficients of the respective rate constants. The relevant bond dissociation energies were calculated, therefore, by using the Arrhenius expression for the rate constant of a unimolecular decomposition

The values of k used in this computation were obtained from experiments carried out at the lowest temperatures. The frequency factor, ν , which was assumed to be constant throughout the whole series, was estimated at 2.1013 sec-1 from the results of the pyrolysis of methyl bromide, $D(CH_3 - Br)$ being taken at 67.5 kcal/ mole. The latter value was determined from thermochemical data in conjunction with the well-established values for $D(CH_3-H)$. This particular estimate of ν compares well with the value of 1 10¹³ sec⁻¹ for the frequency factor of the pyrolysis of Cl₂CBr, which was determined experimentally from the temperature coefficient of the rate constant. The close agreement between

TABLE I.

Compound	D(C - Br) kcal/mole	Compound	D(C – Br) kcal/mole	Compound	D(C - Br) kcal/mole
CH₃Br	(67.5)	CH ₂ Br CH ₂ ClBr CHCl ₂ Br	(67 5) 61.0 53 5	CH3Br CH2Br2 CHBr2	(67.5) 62.5 55 5
CF₃Br	64.5	CCl ₃ Br	49.0	CBr4	49.0

For polybromomethanes the experimental rate constants were divided by the appropriate statistical factor, i.e., the number of bromine atoms in the molecule. These rate constants per bromine atom were used in the above calculations.

these two values of ν is our justification for assuming that the frequency factor remains constant throughout the whole series. The C-Br bond dissociation energies obtained on this basis are listed in Table I.

The outstanding feature of this investigation is the striking decrease in the C-Br bond dissociation energy along the series from CH₃Br to CX₃Br, where X designates a chlorine or bromine atom. One would anticipate a decrease in the C-Br bond dissociation energy with increasing degree of halogenation on account of the increasing steric repulsion between the bulky halogen atoms To illustrate the steric interaction between the various halogens in these compounds, we have given in Fig. 1 the schematic model of a halogenated bromomethane molecule, the circles representing the accepted van der waals radii1 for fluorine, chlorine, and bromine. This diagram reveals clearly that while the overlapping between the fluorine and bromine atoms in CF₃Br is negligible, the overlapping between the chlorine and bromine atoms or two bromine atoms in chlorinated or brominated methyl bromides is quite considerable. Furthermore, it is evident that the extent of the overlap between a chlorine and a bromine atom differs only slightly from that between two bromine atoms It is also apparent that this steric repulsion becomes more pronounced as the number of chlorine or bromine atoms increases.



FIG 1. (r_c =covalent radius, r_w =van der Waals' radius.)

One would expect, therefore, that as a result of this steric repulsion the C-Br bond in Cl₃CBr and CBr₄ would be longer than in CH₃Br. Inspection of the available data on interatomic distances² does not indicate, however, any significant change in the C-Br bond distance in bromomethanes. We conclude, therefore, that there must be another factor compensating for the expected lengthening of the bond due to steric repulsion and leaving the bond strength unaffected *

It seems that this "compression" factor can be interpreted in terms of the results of a recent study of bond energy-bond length relationship by Warhurst and Scanlan.3 These workers proposed a theoretical treatment for molecules of the type MXn, where the M-X bond has a partially ionic character. Assuming that the strength of the M-X bond is unaffected by the number of X atoms in the molecule they deduced that the M-X bond length decreases with increasing value of n. This result is a mathematical consequence of the increasing degeneracy of the system. We suggest, therefore, that the Scanlan-Warhurst effect might account for the observed constancy of the C-Br bond length in bromomethanes.

The observed variation in the C-Br bond dissociation energy along the series CH₃Br to CX₃Br might be attributed, therefore, to the increasing steric repulsion. In addition to this factor, we have to consider the effect of resonance stabilization of the relevant radicals on the C-Br bond dissociation energy. It was suggested^{4, 5} that the stabilization of a radical R might be measured by the difference $D(CH_3-H) - D(R-H)$. On the basis of this assumption we deduce that the stabilization of the Cl₃C. radical amounts to ~ 12 kcal/mole,[†] this value being the difference between $D(CH_3-H)$ and $D(Cl_3C-H)$.

The additional decrease of the C-Br bond dissociation energy in Cl₃CBr as compared with that in CH₃Br would then measure the steric repulsion between the bromine and chlorine atoms which is removed during the dissociation of the Cl₃CBr molecule. We are, however, unable to assess the correction which ought to be introduced in order to account for the possible change in the ionic character of the C-Br bond in Cl₃CBr with respect to that in CH₃Br.

A full account of this work is in course of preparation.

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¹L Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945). ² P. W. Allen and L. E. Sutton, Acta Cryst. **3**, 46 (1950). ^{*} See also R. M. Badger, J. Chem. Phys. **3**, 710 (1935). ³ J. Scanlan and E Warhurst, Trans. Faraday Soc. **45**, 1000 (1949) ⁴ Baughan, Evans, and Polanyi, Trans. Faraday Soc. **45**, 1000 (1949) ⁴ Baughan, Evans, and Polanyi, Trans. Faraday Soc. **45**, 1000 (1949) ⁴ Baughan, Evans, and Polanyi, Trans. Faraday Soc. **47**, 377 (1941). ⁵ M. Szwarc, J. Chem. Phys. **18**, 1660 (1950). ⁴ This amount measures the total stabilization of the Cl₃C · radical which might be made up of two contributions: (i) the "electronic" stabiliza-tion, and (ii) the decrease in the repulsion energy during the process of dissociation, when the closely packed tetrahedral Cl₃C group opens to give the probably planar configuration of the Cl₃C · radical.

The Influence of Aromatic Substitution on the C-Br Bond Dissociation Energy

M. SZWARC, C. H. LEIGH, AND A. H. SEHON Chemistry Department, University of Manchester, Manchester, England (Received March 13, 1951)

HE investigation of the thermal decompositions of benzyl and allyl bromides¹ showed that the respective C-Br bond dissociation energies could be determined by pyrolysing these compounds in an excess of toluene. Under the experimental conditions used in these investigations the bromide molecule dissociates according to Eq. (1)

$$\mathbf{R} \cdot \mathbf{Br} \to \mathbf{R} \cdot \mathbf{+Br}. \tag{1}$$

The bromine atom formed in this process is removed rapidly by reaction (2) A ...

$$C_6H_5.CH_3 + Br \rightarrow C_6H_5 CH_2 + HBr.$$
 (2)

Hence, the rate of the initial dissociation (1) is measured by the

rate of formation of HBr, and the formation of dibenzyl is considered proof of the radical character of reaction (1).

Assuming that the recombination process

$$R+Br\rightarrow R.Br$$

does not require any activation energy, it was concluded that the C-Br bond dissociation energy, D(R-Br), is measured by the activation energy of the unimolecular dissociation process (1).

In the present study this same technique was used for the determination of the changes in the C-Br bond dissociation energies of the substituted benzyl bromides: p-, m-, and o-xylyl bromides, p-, m-, and o-chlorobenzyl bromides, p- and m-bromobenzyl bromides, p- and m-nitrobenzyl bromides, and p- and *m*-nitrilebenzyl bromides. The difference between $D(Ph. CH_2 - Br)$ and $D(Ph_s. CH_2 - Br)$ was measured by the difference in activation energies of reactions (3) and (4)

$$Ph. CH_2. Br \rightarrow Ph. CH_2 \cdot + Br, \qquad (3)$$

$$Ph_s. CH_2. Br \rightarrow Ph_s. CH_2 + Br,$$
 (4)

 $Ph_s.CH_2$ · denoting here the substituted benzyl radical. Assuming that the frequency factor of these unimolecular reactions is not affected by substitution,* we calculated the differences, ΔD 's, between $D(Ph, CH_2 - Br)$ and the values for $D(Ph_s, CH_2 - Br)$ by using the relation

$$\Delta D = 2.3 \cdot R T \cdot \log_{10}(k_s/k_u).$$

 k_u and k_s denote the unimolecular rate constants of reactions (3) and (4), respectively. The results obtained by this method are listed in Table I

The data listed in Table I seem to indicate that the substitution of a hydrogen atom in the benzene ring by a chlorine or bromine atom does not affect the C-Br bond dissociation energy in Ph₈.CH₂.Br, particularly if the substituting halogen atom is in the para or meta position. The apparent increase in ΔD observed in the case of o-chloro-benzyl bromide might be due to orthoeffect affecting the frequency factor, which would then invalidate the calculation for ΔD . The results obtained for the chloro and bromo derivatives are in agreement with the conclusions drawn from the investigation of the pyrolyses of the fluorotoluenes.[†] It appears, therefore, that the influence of the field effect on a bond dissociation energy is negligible even for so highly a polar bond as that in Phs. CH2-Br.

The substitution of a hydrogen atom in the benzene nucleus by a methyl group in the meta position seems to have no effect on $D(Ph_s, CH_2 - Br)$. On the other hand, the introduction of a methyl group in the ortho or para position seems to weaken the corresponding C-Br bond strength. The calculated values for ΔD are 2.0 kcal/mole for o-xylyl bromide and 1.4 kcal/mole for p-xylyl bromide. These two results should be treated however with some reservation, since the ortho-effect might invalidate the calculation in the case of ortho-xylyl bromide and the pyrolysis of p-xylyl bromide exhibited some peculiarities In this connection it is worth mentioning that the C-H bond dissociation energy in *m*-xylene was found to be the same as that in toluene, while $D(o-CH_3, C_6H_4, CH_2-H)$ and $D(p-CH_3, C_6H_4, CH_2-H)$ were

TABLE	I
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Substituted benzyl bromides	ΔD kcal/mole
o-chloro	0.9
<i>m</i> -chloro	01
p-chloro	0.4
m-bromo	03
p-bromo	0.3
o-methyl	2.0
<i>m</i> -methyl	0.0
p-methyl	14
<i>m</i> -nitro	2.1
p-nitro	11
<i>m</i> -nıtrile	1.4
p-nitrile	07