Inductive and Resonance Effects on Deoxymercuration Rates[1a]

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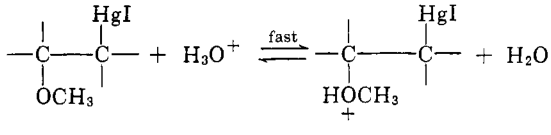
Second-order rate constants, k_2, have been measured for deoxymercuration by nonhalogen acid of fourteen oxymercurials, $RCH(OCH_3)CH_2HgI$, and five oxymercurials, $RCH(OH)CH_2HgI$. For the methyl ethers an excellent correlation (with $\rho^* = -2.77$) between log k_2 and the Taft σ^*'s is obtained when $R = XCH_2$. Compounds in which R is an α,β-unsaturated group give substantial resonance effects. Compounds in which R has other than two α-hydrogen atoms seem to give rise to a Baker–Nathan effect with $n = 0.28$, but the effect is relatively small and the point for R = H is an exception. The data for the alcohols is consistent with a similar pattern. These results preclude a transition state closely resembling the protonated starting state and are consistent with a transition state intermediate between protonated starting state, the olefin–mercuric monoiodide complex plus methanol, and the carbonium ion plus methanol.

The mechanism of deoxymercuration reaction has been discussed in a series of previous papers.[2-4] It is summarized in equations 1–3 for the special case of a methoxymercurial deoxymercurated by nonhalogen acid. (Equation 3 represents a series of fast steps.) The electron distribution in the transition state can probably be represented by a resonance hybrid involving the protonated starting state, I; the olefin-mercuric iodide complex, II; and the carbonium ion, III.



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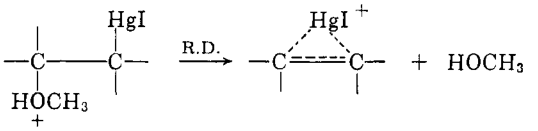

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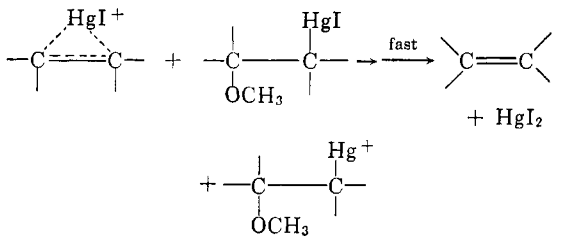

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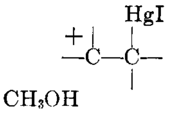

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In the present paper deoxymercuration rates are reported for a series of compounds $R—CH(OCH_3)CH_2HgI$. Relative rates are interpreted in terms of inductive, resonance, and Baker–Nathan effects. The size of these effects suggests that II and/or III contribute substantially to the transition state structure.

Results

Deoxymercuration rates have been determined at 25.0 ± 0.1° for fourteen methoxymercurials in aqueous solution containing 2% of methanol. These rates are first order in acid and first order in substrate. Second-order rate constants, k_2, are collected in Table I. Each of the values shown is the average of at least four determinations and the average deviation from the mean value is shown.

TABLE I
RATE CONSTANTS FOR DEOXYMERCURATION OF COMPOUNDS $RCH(OCH_3)CH_2HgI$

No.	R	k_2, l. mole^{-1} sec.$^{-1}$	Δ, l. mole^{-1} sec.$^{-1}$
1	C_2H_3	17.9	0.4
2	C_6H_5	12.16[a]	.35
3	neo-C_5H_{11}	2.09	.08
4	C_2H_5	1.21	.10
5	*i*-C_3H_7	1.18	.15
6	CH_3	0.658[b]	.083
7	*t*-C_4H_9	.539	.047
8	$C_6H_5CH_2$	6.86×10^{-2}	6×10^{-4}
9	H	3.35×10^{-2}[c]	8×10^{-4}
10	$HOCH_2$	2.21×10^{-2}	1×10^{-4}
11	$CH_3CH(OH)$	1.35×10^{-2}	1×10^{-4}
12	CH_3OCH_2	9.33×10^{-3}	1×10^{-4}
13	$C_6H_5OCH_2$	4.37×10^{-3}	2×10^{-4}
14	$CNCH_2$	1.1×10^{-4}	1×10^{-5}

[a] Taken from the M.S. thesis of Bruce Eisen, University of Minnesota, 1962, p. 8. [b] Ref. 2. [c] Ref. 4.

The logarithms of these rate constants were plotted aganst the Taft σ^*'s.[5] The plot is shown in Fig. 1. The values of σ^* used were all those of Taft[5] except that for $R = CH_2OCH_3$, for which a value of 0.65 g. is now preferred,[6] that for $R = CH(OH)CH_3$ which was estimated to be 0.45 by addition of known values,[5] and that for R =

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[1] (a) This research was supported by the Air Force Office of Scientific Research through Contract No. AF 49 (638)711. Reproduction is permitted for any purpose of the U.S. Government; (b) to whom requests for reprints should be sent.

[2] M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959).

[3] M. M. Kreevoy and F. R. Kowitt, *ibid.*, **82**, 739 (1960).

[4] M. M. Kreevoy and L. T. Ditsch, *ibid.*, **82**, 6127 (1960).

[5] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., Chap. 13.

[6] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959) (footnote 12).

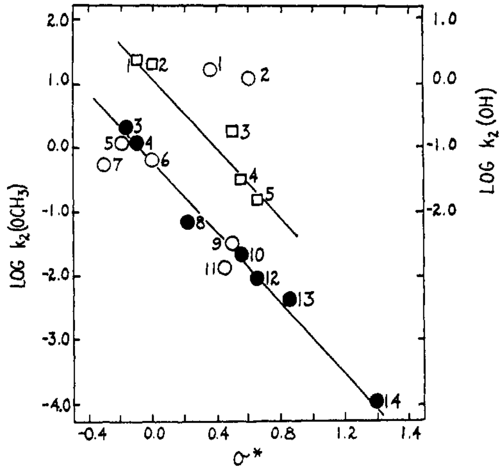

Fig. 1.—Plots of log k_2 *vs.* σ^*. The solid circles are points for R = XCH_2, used to define ρ^*. The open circles represent rates for methoxymercurials in which $n = 2$. The squares represent rates for hydroxymercurials and are referred to the ordinate indicated on the right. Both sets of points are referred to the same scale on the abscissa. The numbers identify the substituents and correspond to the numbers in Tables I and II.

C_2H_3, which was assumed to be identical with that for R = $CH_3CH = CH$—. Inspection of Fig. 1 reveals that all of the points for which R = XCH_2 define a straight line of excellent precision. The slope of this line (the Taft ρ^{*5}) is -2.77 as defined by the method of least squares.[7] The average deviation of a point from the line is ± 0.12 log units, the correlation coefficient is 0.996, and the 50% confidence limits on the slope are ± 0.02. The largest deviation of a point from the line, pt. 8, is 0.32 log unit. Several of the larger deviations are substantially larger than the experimental uncertainty in the measured quantity but these measures of uncertainty compare favorably with those of the better correlations reported by Taft.[5]

On the other hand, it is plain that the points corresponding to the phenyl group and the vinyl group are widely deviant from the line defined by points XCH_2. Points corresponding to several alkyl groups having other than two α-hydrogen atoms also do not fit the line well. The former react too rapidly for correlation and the latter are too slow. Effects of this sort have previously been associated with resonance and Baker-Nathan effects.[8,9]

Rates have been correlated by equation 4 for those substituents which are not α,β-unsaturated.[8]

$$\log (k_2/k_2^\circ) = \rho^*\sigma^* + h(\Delta n) \qquad (4)$$

In equation 4, k_2 is the second-order rate constant for deoxymercuration of a compound, R—CH(OCH_3)CH_2HgI; k_2° is the analogous rate constant for the compound in which R is methyl. The quantity $\rho^*\sigma^*$ represents the inductive contribution to relative reactivity is ρ^*; the slope previously obtained for R = XCH_2. The Baker–Nathan contribution to relative reactivity is represented by $h(\Delta n)$, in which h is an empirical parameter representing the Baker–Nathan contribution per α-hydrogen and Δn is n, the number of α-hydrogens in the substituent giving rise to k_2 less n_0, the number in the standard substituent. In the present work n_0 is three. A value of h was obtained for each of the five substituents in which n is other than two by equating the deviation of the point from the previously defined line to $h(n - 2)$. The average value is 0.22 ± 0.16. For X = H, h is -0.03 and if this datum is omitted the average h is 0.28 ± 0.14. The average deviation of points calculated from equation 4 for substituents in which n is other than two is 0.24 if all five are included, or 0.15 if R = H is omitted and 0.28 is used for h.

It is obvious by inspection of Fig. 1 that the inclusion of the second term in equation 4 cannot be justified on the basis of the improvement of fit obtained for the saturated alkyl groups. Excluding the point for R = t-C_4H_9, all of the data could be moderately well correlated by the first term alone. Including the second term, R = H must be excluded in order to get a good fit. It can only be said that the data do not exclude the second term. If a Baker–Nathan term is used, 0.28 is probably a better value for h than 0.22, and the point for R = H must be considered deviant (by 0.66 log units) for other reasons.

The effect of conjugation in the cases R = C_6H_5 and C_2H_3 was equated to the difference between the observed log (k_2/k_2°) and that calculated from equation 4. It is $+3.54$ log units for R = C_6H_5 and $+2.76$ log units for R = C_2H_3. In keeping with past practice,[10] the formal α-hydrogen of C_2H_3 has been counted although the most probable conformation of the transition state would minimize any Baker–Nathan effect involving this hydrogen atom. As noted in other systems,[10] the resonance effects to which the two unsaturated groups gave rise are similar. It has been noted before[10] that the resonance effect to which a single unsaturated group gives rise is about ten times h and a factor of 13 has been suggested on a theoretical basis.[11] The average of the two resonance effects obtained above is 3.15 log units, which is eleven times the best value of h. This is the best justification available for the inclusion of the Baker–Nathan term in equation 4.

Rates of acid deoxymercuration for five hydroxymercurials, RCH(OH)CH_2HgI, have also been measured. The mean values of k_2 for these compounds are listed in Table II along with the average

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[7] C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, 1954, p. 21.

[8] M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77**, 5590 (1955).

[9] M. M. Kreevoy, *Tetrahedron*, **5**, 233 (1959).

[10] M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4011 (1957).

[11] M. M. Kreevoy and H. Eyring, *ibid.*, **77**, 5121 (1957).

TABLE II

RATE CONSTANTS FOR DEOXYMERCURATION OF COMPOUNDS $RCH(OH)CH_2HgI$

No.	R	k_2 (obs.), l. mole^{-1} sec.$^{-1}$	Δ, l. mole^{-1} sec.$^{-1}$
1	C_2H_5	2.31	0.08
2	CH_3	2.13[a]	.12
3	H	0.190	.012
4	$HOCH_2$	3.30×10^{-2}	1.3×10^{-3}
5	CH_3OCH_2	1.58×10^{-2}	4×10^{-4}

[a] Taken from ref. 2.

deviations for the mean. There are not enough of these data to treat them independently but their logs are plotted against σ^* in Fig. 1. The correlation line shown has the same slope as that obtained for the methoxymercurials. It is plain that these rates are consistent with the parameters ρ^* and h obtained for the methoxymercurials except that the point for R = H is even more widely divergent in the positive direction.

Discussion

The results cited above show unambiguously that the deoxymercuration transition state cannot *generally* be considered a slightly modified protonated starting state. The latter should give a much less negative value of ρ^* than that observed here and no substantial resonance effects at all.

Equilibria in aqueous solution in which a unit formal charge is produced on an atom two atoms removed from the substituent give rise to ρ^* values around 1.7, the sign depending on the sign of the charge. ρ^* is 1.4 for acid dissociation of alcohols, RCH_2OH[12]; 1.7 for the acid dissociation of carboxylic acids, RCOOH[5]; and about -2.0 for the protonation of amines, $RCH_2N(CH_3)_2$.[13] Equilibria in which a formal charge is produced on the atom adjacent to the substituent give ρ^* values around 3.3, the sign again varying with the sign of the charge. ρ^* for protonation of amines, $R_1R_2R_3N$, is -3.2[14]; for acid dissociation of mercaptans, RSH, it is 3.4.[15] Several correlations are available for rates involving cationic intermediates. When the transition states would seem to resemble an intermediate with the positive charge on the atom adjacent to the substituent ρ^* has a value between -3.3 and -4.3.[5,16] By comparison it is clear that the ρ^* obtained in the present case is considerably too large to permit a transition state closely resembling the protonated starting state. On the other hand, it is somewhat too small for a transition state closely resembling the cation, III. It is not possible to estimate a value of ρ^* for a transition state resembling II so no quantitative assignment of weights to the three structures can be made.

Current theory would not predict large deviations from correlation with σ^* for α,β-unsaturated groups if the transition state closely resembled I. Reactions producing a unit charge separated by a saturated carbon atom from an unsaturated group do not usually lead to such deviations.[5] The benzyl group, as a substituent, is well correlated in reaction series where a charge is produced on the atom adjacent to the substituent.[5] On the other hand, the observed resonance effects seem to be too small if a transition state closely resembling III is assumed. The resonance effect of a single α,β-unsaturated substituent on an acetal hydrolysis rate is over five log units compared to about three in the present case. There is a lack of good analogy for the resonance effect to which a transition state like II would give rise. In addition, the degree to which the introduction of the unsaturated groups may alter the electronic structure of the transition state is now known.[9] These factors again preclude the assignment of quantitative weights to the various contributing structures in the transition state.

A very small secondary hydrogen isotope effect had previously been found for the deoxymercuration of $CH_3OCH_2CH_2HgI$.[4] Theoretical considerations lead to the prediction of $k_H/k_D > 1$ if the transition state resembled III and $k_H/k_D < 1$ if it resembled II. The very small effect actually found was most simply explained by assuming that the transition state closely resembled I. The present work, however, excludes this possibility. It is possible that roughly equivalent contributions from *both* II and III to the transition state would produce the observed k_H/k_D. A transition state structure made up of roughly equivalent contributions from I, II, and III would probably satisfy both the isotope effect and the relative reactivities, and this is now thought to be the most likely situation.

There is no obviously correct reason for the failure of the datum for R = H to fit equation 4, although there are several possibilities. One is a steric effect, either direct or on the solvation, if R is larger than hydrogen. This is in the right direction but is made less likely by the excellent fit obtained with such large groups as neopentyl and *t*-butyl. Another possibility is a significant change in the electronic structure of the transition state accompanying the introduction of substituents other than hydrogen.[9] A third possibility is that the hydrogen atom as a substituent produces inductive effects that are not well correlated by the Taft–Hammett type of equation.[5,16] At present there seems to be no sound basis for choosing among these alternatives.

Experimental[17]

Kinetic Measurements.—First-order rate constants were obtained from semilogarithmic plots of absorbance at 2800

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[12] D. Ballinger and F. A. Lang, *J. Am. Chem. Soc.*, **82**, 795 (1960).

[13] Estimated from data cited by Hall, ref. 14.

[14] H. K. Hall, *J. Am. Chem. Soc.*, **79**, 5441 (1957).

[15] M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *ibid.*, **82**, 4899 (1960).

[16] R. W. Taft, Jr., private communication.

[17] All melting points are corrected.

A. *vs.* time as previously described.[2] In all cases except for R = CH_2CN second-order rate constants were obtained by dividing first-order rate constants by the hydronium ion concentration. For the slower reactions the hydronium ion was provided by perchloric acid. For faster reactions the hydronium ion was provided by acetic acid–sodium acetate buffers. In the buffer solutions the ionic strength effect on the dissociation constant of acetic acid was taken into account by using the Debye–Hückel limiting law for activity coefficients, as previously described.[2] In the case of R = CH_2CN the deoxymercuration was so slow that rates were measured in 1.0 *M* to 2.4 *M* perchloric acid. Second-order rate constants were obtained by dividing the first-order rate constants by h_0.[18] They showed no systematic trend and the scatter is reflected in the uncertainty listed in Table I. Solvents, acids, and bases were prepared as previously described.[2]

Materials. 4-Iodomercuri-3-methoxy-1-butene, m.p. 34.5–35.5°, was obtained by dissolving the corresponding chloromercurial[19] in carbon tetrachloride and extracting with three portions of 15% aqueous sodium iodide. The carbon tetrachloride layer was then dried and the carbon tetrachloride removed under vacuum at room temperature. The residual oil was dissolved in methanol, water was added to just short of the cloud point, and the solution was cooled in a refrigerator overnight to obtain crystalline material.

Anal. Calcd. for C_5H_9HgIO: C, 14.55; H, 2.20. Found: C, 14.80; H, 2.31.

2-Phenyl-2-methoxyethylmercuric iodide was prepared by the method of Wright,[20] and had a m.p. of 30–31°. This material has previously been reported with a m.p. of 49–52°.[21] To demonstrate its identity it was converted to the known acetate, m.p. 64–66° (reported,[20] 70°), with silver acetate, and the latter was converted to the known bromide with sodium bromide, m.p., 63–65° (reported,[20] 63°). The infrared spectra of these compounds corresponded to expectations and that of the bromide was essentially identical with that of the iodide, as expected. The iodide also had a suitable n.m.r. spectrum. In another connection, the 2-deutero, 1,1-dideutero, and1 ,1,2-trideutero derivatives of the iodo compound were also prepared from the correspondingly deuterated styrenes. These had identical melting points and suitable n.m.r. spectra.[22] We are at a loss to explain the discrepancy in the melting points.

Anal. Calcd. for $C_9H_{11}HgIO$: C, 23.36; H, 2.40. Found: C, 22.99; H, 2.65.

4,4-Dimethyl-2-methoxypentylmercuric iodide was an oil that could not be completely purified. Inorganic mercury compounds were removed from its chloroform solution by repeated extraction with aqueous sodium iodide. The chloroform and any volatile organic impurities were removed by prolonged evacuation at room temperature. From the analytical data some nonvolatile organic contaminants remained. The oil could not be distilled without decomposition. The contamination did not seem to interfere with the kinetic measurements.

The compound was prepared from mercuric acetate, methanol, and 4,4-dimethyl-1-pentane,[23] by the method of Wright.[20]

Anal. Calcd. for $C_8H_{17}HgIO$: C, 21.04; H, 3.76. Found: C, 22.14; H, 3.69.

4,4-Dimethyl-1-pentene was prepared by pyrolysis of 4,4-dimethyl-1-pentyl acetate[24] at 480° and had an infrared spectrum identical with the authentic material.[25]

2-Methoxybutylmercuric iodide was prepared by the method of Wright.[20] It was an undistillable oil and could only be purified by extraction of its chloroform solution with aqueous sodium iodide.

Anal. Calcd. for $C_5H_{11}HgIO$: C, 14.47; H, 2.65. Found: C, 14.46; H, 2.64.

3-Methyl-2-methoxybutylmercuric iodide and 3,3-dimethyl-2-methoxybutylmercuric iodide were prepared and purified similarly and were also undistillable oils.

Anal. Calcd. for $C_6H_{13}HgIO$: C, 16.78; H, 3.03. Found: C, 17.07; H, 3.15.

Anal. Calcd. for $C_7H_{15}HgIO$: C, 18.98; H, 3.39. Found: C, 19.42; H, 3.51.

3-Hydroxy-2-methoxypropylmercuric iodide was prepared by the method of Whitehead,[26] and purified by recrystallization from toluene and washing with petroleum ether (b.p. 60–68°) m.p. 79–80.5°.

Anal. Calcd. for C_4H_9HgIO: C, 11.53; H, 2.18. Found: C, 11.21; H, 2.14.

3-Hydroxy-2-methoxybutylmercuric iodide was prepared from the corresponding chloride by extraction of its carbon tetrachloride solution with aqueous sodium iodide. It was an undistillable oil, but the method of preparation apparently removed the water of hydration that was present in the chloride.

Anal. Calcd. for $C_5H_{11}HgIO_2$: C, 13.96; H, 2.58. Found: C, 14.24; H, 2.77.

3-Hydroxy-2-methoxybutylmercuric chloride was prepared by the method of Whitehead,[26] and was also an undistillable oil. It was cloudy and seemed to be firmly hydrated. Its infrared spectrum showed the water bending frequency (at 1730 cm.$^{-1}$) as well as the O—H stretching frequency at 3400 cm.$^{-1}$. By analysis it was a trihydrate. Its structure is supported by its conversion to the anhydrous iodide.

Anal. Calcd. for $C_5H_{11}ClHgO_2 \cdot 3H_2O$: C, 15.27; H, 4.36. Found: C, 14.82; H, 4.39.

2,3-Dimethoxypropylmercuric iodide was prepared from mercuric nitrate monohydrate (17.13 g., 0.05 mole) in 100 ml. of methanol. Methanolic potassium methoxide was added until a slight precipitate appeared. Then 3-methoxypropene was added until the precipitate was discharged. This process was repeated until all the ether (3.6 g., 0.05 mole) had been added. Sodium iodide (7.5 g., 0.05 mole) was then added as a 10% aqueous solution, which caused the precipitation of a small amount of black precipitate. After this was filtered off, the solution was saturated with carbon dioxide and the methanol removed by an air stream. The residual oil was purified by repeated extraction of its chloroform solution with aqueous sodium iodide but it would not crystallize.

Anal. Calcd. for $C_5H_{11}HgIO_2$: C, 13.94; H, 2.57. Found: C, 14.11; H, 2.83.

3-Phenoxy-2-methoxypropylmercuric iodide was prepared by the method of Wright,[20] purified by repeated extraction of its chloroform solution with aqueous sodium iodide, and recrystallized from mixtures of benzene and ethyl acetate with petroleum ether, m.p. 47–47.5°.

Anal. Calcd. for $C_{10}H_{13}HgIO_2$: C, 24.37; H, 2.64. Found: C, 24.44; H, 2.65.

3-Cyano-2-methoxypropylmercuric iodide was prepared by the method of Wright[20] and purified by repeated extraction of its chloroform solution with aqueous sodium iodide. It was a solid and was recrystallized from toluene, m.p. 89–90°.

Anal. Calcd. for C_5H_8HgINO: C, 14.11; H, 1.89. Found: C, 13.82; H, 1.83.

Because the σ^* value for the cyanomethyl group is more positive than that of a hydrogen atom,[5] it was necessary to verify the direction of addition of methoxymercuric acetate

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[18] F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

[19] K. H. McNeeley and G. F. Wright, *J. Am. Chem. Soc.*, **77**, 2553 (1955).

[20] G. F. Wright, *ibid.*, **57**, 1993 (1935).

[21] G. Spengler and A. Weber, *Brennstoff-Chem.*, **40**, 22 (1958).

[22] B. Eisen, M.S. thesis, University of Minnesota, 1962.

[23] F. C. Whitmore and A. H. Homeyer, *J. Am. Chem. Soc.*, **55**, 4555 (1933).

[24] A. J. Birch, *J. Chem. Soc.*, 2721 (1949).

[25] American Petroleum Institute Project 44 Infrared Spectra 1063 and 1064.

[26] C. Whitehead, *J. Am. Chem. Soc.*, **80**, 2178 (1958).

to 3-cyanopropene. This was done by reducing the corresponding iodide (70 g., 0.164 mole) in 300 ml. of water with 350 g. of 2% sodium amalgam.[27] After several hours of agitation the solid disappeared. The aqueous layer was separated and treated with benzene for 24 hr. in a continuous liquid-liquid extractor. The benzene layer was dried and distilled through a 10-in. spiral wire column yielding 3.05 g. (24%) of 3-methoxybutyronitrile, b.p. 172°, $n^{25}D$ 1.4084 (reported,[28] b.p. 169–170°, $n^{20}D$ 1.4094). These physical constants do not distinguish it from 4-methoxybutyronitrile; reported,[29] b.p. 173°, $n^{20}D$ 1.4087. The n.m.r. spectrum was completely unambiguous, however, consisting of a doublet at τ, 8.74 ($\underline{CH_3}$—CH—), a doublet at τ, 7.53 (—CH—$\underline{CH_2}$—CN), an intense singlet at τ, 6.63 ($\underline{CH_3}$—O—), and a low lying multiplet around τ, 6.5 (CH_3—$\underline{CH}$—CH_2—). The relative intensities and the coupling constants were also appropriate to the suggested structure. The spectrum of 4-methoxybutyronitrile should include no doublets and two triplets in addition to a low lying multiplet at the high field end of the spectrum.[30]

2-Hydroxybutylmercuric iodide was prepared by the method of Hofmann and Sand[31] and purified by crystallization from mixtures of toluene with low-boiling petroleum ether. It had m.p. 42°.

Anal. Calcd. for C_4H_9HgIO: C, 11.99; H, 2.26. Found: C, 12.11; H, 2.42.

2-Hydroxy-3-methoxypropylmercuric iodide was prepared by the method described for 1,2-dimethoxypropylmercuric iodide. It was a solid and was purified by crystallizing first from a mixture of ethyl acetate with petroleum ether and then twice from diethyl ether, m.p. 40–41°.

Anal. Calcd. for $C_4H_9HgIO_2$: C, 11.53; H, 2.18. Found: C, 11.04; H, 2.27.

3-Phenyl-2-methoxypropylmercuric iodide, m.p. 58° (reported,[32] 58.6°) and 2-hydroxyethylmercuric iodide, m.p. 145° dec., (reported,[33] 147°) were previously known compounds.

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[27] L. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1955, p. 370.

[28] P. Bruylants, *Bull. soc. chim. Belges*, **31**, 175 (1922).

[29] A. Karvonen, *Ann. acad. sci. Fennicae*, **20**, No. 14 (1923).

[30] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chap. 6.

[31] K. A. Hofmann and J. Sand, *Ber.*, **33**, 1354 (1900).

[32] T. A. Geissman and R. M. Horawitz, *J. Am. Chem. Soc.*, **73**, 5759 (1951).

[33] K. A. Hofmann and J. Sand, *Ber.*, **33**, 1641 (1900).

The Application of Simple Equations for Calculating Bond Dissociation Energies to Thermal Degradation of Fluorocarbons

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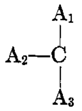
Bond dissociation energies of fluorocarbon compounds were calculated by means of simple equations that relate the strength of the bond in question with the molecular structure. The bond dissociation energies determined experimentally for relatively simple fluorocarbons agree within 2 kcal. with the corresponding calculated values. These equations can be used to explain the relative thermal stability of more complicated fluorocarbon compounds and to help anticipate the nature of the pyrolyzate produced assuming initial rupture to occur at the weakest bond. The pyrolysis of cyclobutanes are considered for the purpose of illustration. The thermal degradation of poly(tetrafluoroethylene) is also discussed and it is suggested that the "unzippering" process might occur *via* elimination of CF_2 fragments that subsequently couple to give C_2F_4 rather than *via* depolymerization of CF_2=CF_2 units directly.

Simple but reliable equations for calculating bond dissociation energies of hydrocarbon compounds were deduced empirically as described in proceding publications.[1,2] The bond dissociation energy (D) is given in terms of the characteristic binding coefficients (ϵ) of the two groups comprising the bond in question. Thus for the bond R_i—R_j

$$D = 71\epsilon_i\epsilon_j \qquad (1)$$

It was also shown that the ϵ of the group



$$A_2\text{—}\overset{\displaystyle A_1}{\underset{\displaystyle A_3}{C}}$$

is given by

$$\epsilon = 0.43 + 0.162(\epsilon_1 + \epsilon_2 + \epsilon_3) \qquad (2)$$

provided that the groups (or atoms) A_1, A_2, A_3 do not have a center of unsaturation α to one of the central carbon atoms. The ϵ_g of radicals such as $\cdot CH_2C_6H_5$, $\cdot CH(C_6H_5)_2$, and $\cdot CH_2CH$=CH_2 cannot be calculated by equation 2, but rather must be determined experimentally.[1,2] Once the ϵ value is determined for one member of a homologous series such as $CR_1R_2A_1$ (or $CR_1A_1A_2$) where A is a group with a center of unsaturation α to the central carbon atom, the ϵ value for all other members of of that series can be calculated by means of equation 2.

Only a relatively few key experimental bond dissociation energies of this sort are available from thermal degradation studies. However, the ap-

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[1] L. A. Errede, *J. Phys. Chem.*, **64**, 1031 (1960).

[2] (a) L. A. Errede, *ibid.*, **65**, 2262 (1961); (b) equation 8 of this publication should read: $\log k_2/k_1 = 4.00(\epsilon_1 + \epsilon_2) - 2.85 - 6.44\,\epsilon_g$.