The Effect of Structure on Acid-Induced Deoxymercuration Rates. Variation in the Alcohol Component[1]

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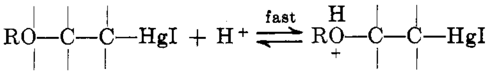
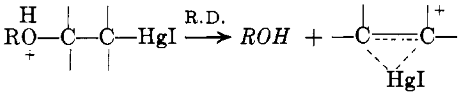
The aqueous acid induced deoxymercuration rates of 14 oxymercurials, $ROCH_2CH_2HgI$, have been measured and combined with two previously available. The rates cover a range of a factor of over 20. No over-all correlation with the Taft σ^* is obtained, but a very limited correlation suggests a ρ^* of ~ -1.4. Steric factors and possibilities for internal hydrogen bonding also seem to influence the rates.

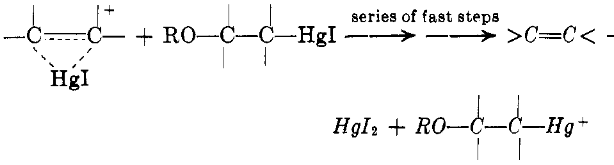
In previous papers[2,3] the mechanism of the deoxymercuration reaction has been elucidated and the effect on the rate of a variety of substituents R, in $RCH(OCH_3)CH_2HgI$, has been determined.[4] The preferred mechanism and stoichiometry are shown in eq. 1–3. (Italic substances are final products.) This work has suggested substantial contributions to the transition state hybrid from the protonated starting state. Such a hypothesis requires that the rate be sensitive to the structure of the alcohol component of the oxymercurial, R in $ROCH_2CH_2HgI$. However, a previous report[5] indicates that the rate of deoxymercuration of the analogous 2-alkoxycyclohexylmercuric chlorides is insensitive to the structure of the alkoxyl group.



$$\mathrm{RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgI} + H^+ \overset{\text{fast}}{\rightleftharpoons} \mathrm{R\overset{H}{\underset{+}{O}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgI} \qquad (1)$$



$$\mathrm{R\overset{H}{\underset{+}{O}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgI} \xrightarrow{\text{R.D.}} \mathit{ROH} + {-}\overset{|}{C}\overset{HgI}{\text{=====}}\overset{|+}{C}{-} \qquad (2)$$



$$-\overset{|}{C}\overset{HgI}{\text{=====}}\overset{|+}{C}- + \mathrm{RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgI} \xrightarrow{\text{series of fast steps}} \longrightarrow >\!C\!=\!C\!< + \mathit{HgI_2} + \mathit{RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Hg^+} \qquad (3)$$

The present paper reports the deoxymercuration rate constants, k_2, for 14 2-alkoxyethylmercuric iodides, measured spectrophotometrically at 25° in aqueous perchloric acid (containing 2% of methanol). Two more of such rate constants were available from previous work. A modest variation in k_2 with structure was observed, with a factor of over 20 separating the fastest from the slowest. A number of systematic structural effects on reactivity are discernable. The results are compatible with the previous hypothesis about the structure of the transition state.

Results

All the compounds in question were prepared, essentially, by the method of Wright,[6] as outlined in eq. 4 and 5. Many of the yields were poor, but no attempts were made to improve them as only miniscule amounts of material are required for this sort of kinetic study. The identity and purity of these products were verified by analysis and their spectroscopic properties.

$$ROH + Hg(OAc)_2 + CH_2{=}CH_2 \longrightarrow ROCH_2CH_2HgOAc + HOAc \qquad (4)$$

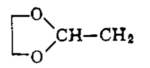
$$ROCH_2CH_2HgOAc + I^- \longrightarrow ROCH_2CH_2HgI + OAc^- \qquad (5)$$

The progress of the reaction was followed, as previously described,[7] by following the buildup of optical density at 2800 Å. Pseudo-first-order rate constants, k_1, were obtained from a slightly modified form of the integrated first-order rate law, shown in eq. 6.[7] (The optical density at time, t, is D_t.) Plots of log $(D_\infty - D_t)$ *vs.* t showed no significant departures from linearity up to 90% of completion in most cases. Values of k_1 were obtained from these plots.[7] Values of k_2, given by $k_1/(H^+)$, were shown to be invariant, within the precision of the measurements, under at least a five-fold change in (H^+) for each compound. At least four values of k_1 and k_2 were obtained for each compound, and the average deviation from the mean value was usually about ±5%. The mean k_2-values are shown in Table I, as a function of R.

$$2(t - t_0)k_1 = \ln [(D_\infty - D_0)/(D_\infty - D_t)] \qquad (6)$$

Table I

Rate Constants for Deoxymercuration of $ROCH_2CH_2HgI$ in Aqueous Perchloric Acid at 25°

No.	R	$10^2\,k_2$, l. mole^{-1} sec.$^{-1}$
1	t-C_4H_9	33.2
2	H	19.0[a]
3	*sec*-C_4H_9	10.1
4	i-C_3H_7	8.7
5		6.4
6	i-C_4H_9	6.1
7	n-C_4H_9	5.2
8	C_2H_5	4.96
9	$HOCH_2CH_2$	4.51
10	CH_3	3.32[b]
11	$CH_3OCH_2CH_2$	3.23
12	$CH_3COCH_2CH_2$	2.63
13	$C_6H_5CH_2$	1.81
14	CH_3CO	1.68
15	$NCCH_2CH_2$	1.46
16	F_3CCH_2	1.44

[a] Taken from ref. 4. [b] Taken from M. M. Kreevoy and L. T. Ditsch, *J. Am. Chem. Soc.*, **82**, 6127 (1960).

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[1] This work was supported by the U. S. Air Force, Office of Scientific Research, through Grant AF-AFOSR-16-63. Reproduction is permitted for any purpose of the U. S. Government.

[2] M. M. Kreevoy and F. R. Kowitt, *J. Am. Chem. Soc.*, **82**, 739 (1960).

[3] M. M. Kreevoy and B. M. Eisen, *J. Org. Chem.*, **28**, 2104 (1963).

[4] L. L. Schaleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *ibid.* **27**, 3421 (1962).

[5] A. Rodgman, D. A. Shearer, and G. F. Wright, *Can. J. Chem.*, **35**, 1377 (1957).

[6] G. F. Wright, *J. Am. Chem. Soc.*, **57**, 1993 (1935).

[7] M. M. Kreevoy, *ibid.*, **81**, 1099 (1959).

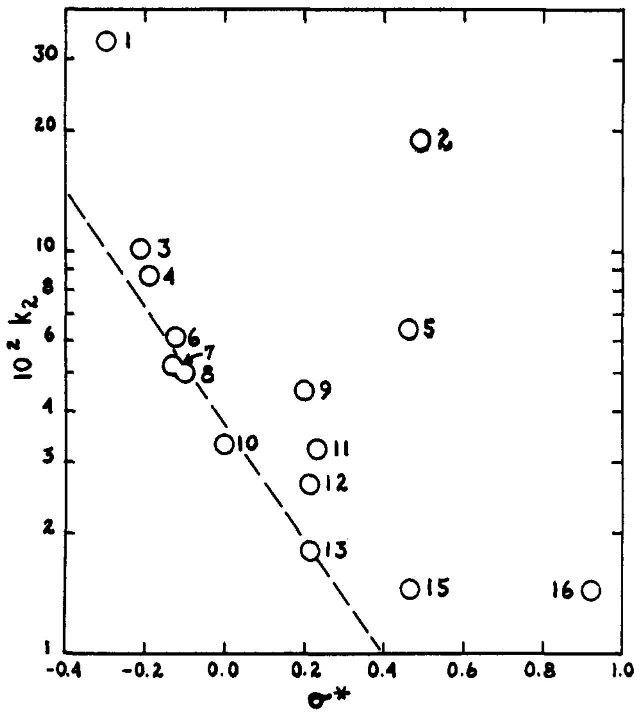


Figure 1.—A semilogarithmic plot of k_2 *vs.* the Taft σ*. The numbers identify the alkyl groups, and refer to the numbers in Table I. Values of σ* are those of Taft[11] except for substituents **5**, **9**, **11**, **12**, and **15**. For substituents **9**, **11**, **12**, and **15**, all groups of the type CH_2CH_2X, values were obtained by dividing the σ* of the group, CH_2X, by 2.8. [For CH_2OCH_3 a value of 0.65 was used, as suggested by R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, 81, 5343 (1959)]. For substituent **5** the value for CH_3OCH_2, 0.65, was multiplied by 2.0 and divided by 2.8, giving 0.46. The point **14**, for R, CH_3CO, σ*, 1.65, was omitted to avoid expanding the absissa. The dashed line was obtained from points **6**, **7**, **8**, **10**, and **13**, and has a slope, ρ*, of −1.4.

Eyring enthalpies of activation, ΔH^*, were obtained for the compounds with R, *n*-butyl; and R, 2-methoxyethyl. In each case rates were measured over a 63° temperature range, 0–63°. Fifteen measurements were made for the former and 20 for the latter. These were fitted to eq. 7[8] by the method of least squares.[9]

$$R \ln (k_2/T) = -\Delta H^*/T + C \qquad (7)$$

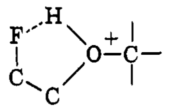
For R_1, normal butyl, ΔH^* was 16.5 ± 0.3 kcal. mole^{-1} and ΔS^* was −8.8 ± 1.0 cal. mole^{-1} deg.$^{-1}$. For R, 2-methoxyethyl, ΔH^* was 19.0 ± 0.2 kcal. mole^{-1} and ΔS^* was −1.5 ± 0.8 cal. mole^{-1} deg.$^{-1}$. Both entropies were estimated from the corresponding enthalpies, the k_2 values at 25°, and the usual thermodynamic equalities.[10] The cited uncertainties are 50% confidence limits. The plots of k_2/T *vs.* $1/T$ showed no discernable, systematic curvature, and the deviations from the correlation line were of the order of magnitude of the experimental imprecision.

Discussion

Figure 1 shows a plot of log k_2 *vs.* the Taft σ*-parameter of the group, R.[11] The inductive parameter, σ*, may be regarded as the effective Pauling electronegativity[12] of the substituent, R.[13] It is obvious that there is no precise, general correlation between these variables. Qualitatively, most of the data can be explained on the basis of three effects: (1) an inductive effect proportional to σ* with ρ*, ∼−1.4; (2) a steric acceleration; and (3) an acceleration due to internal hydrogen bonding in the transition state with appropriate substituents.

The first effect is thought to govern relative reactivities almost completely in the series, benzyl, methyl, ethyl, *n*-butyl, and isobutyl. It is from this series that the suggested ρ* is obtained. As the bulkier secondary and tertiary alkyl groups are introduced telescopically increasing steric accelerations are observed. This behavior is qualitatively similar to that observed in ketal hydrolysis.[14]

Steric and inductive effects alone, however, will not account for the results obtained with substituents capable of internally hydrogen bonding, as shown in structures I, II, III, or IV. The problem is illustrated by the β,β,β-trifluoroethyl group, which has steric requirements resembling the substituents defining the line, but deviates from the line by nearly a factor of ten; or by the series, **9**, **11**, **12**, and **13**, which have nearly identical σ*-values, modest, similar steric requirements, but rates which differ by over a factor of two in the extreme cases. These anomalies can be explained if it is assumed that internal hydrogen bonding of the sort shown enhances the rate. In nonpolar solvents, such hydrogen bonding has been shown to be significant for 2-chloroethanol,[15] 2-methoxyethanol,[16] 2,2,2-trifluoroethanol,[17] and 2-phenylethanol,[15,18] which is sterically somewhat analogous to the 2-cyanoethyl substituent. The use of the polar, hydrogen-bonding solvent, water undoubtedly reduces the importance of these interactions, but the fact that the donor O–H group of the transition state carries a substantial positive charge re-emphasizes them.



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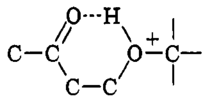

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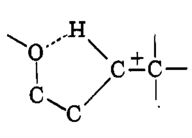

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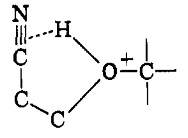

IV

If this explanation is correct, the acceleration due to internal hydrogen bonding should be accompanied by positive changes in ΔH^*, because the internal hydrogen bonds would probably be less exothermic

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(8) M. M. Kreevoy, "Investigations of Rates and Mechanisms of Reactions," S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Part II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 1392.

(9) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industries," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 36-40.

(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 99-101.

(11) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., Chapter 13.

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(16) L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

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(18) M. Oki and H. Iwamura, *Tetrahedron*, **16**, 139 (1961).

than those to water,[16] and positive changes in ΔS^*, because less water need be immobilized to form the transition state. This prediction is born out by the ΔH^* and ΔS^* values for the compounds with the otherwise similar *n*-butyl and 2-methoxyethyl substituents. The observed difference in ΔS^*, 7 cal. mole^{-1} deg., is of about the proper size, since the molar entropy of freezing of liquid water at 25° is 5.5 cal. mole^{-1} deg.$^{-1}$.[19]

This leaves only two k_2-values unexplained, that for H as a substituent and that for CH_3CO as a substituent. Both are substantially faster than would be expected from the foregoing considerations, but in each case there is a ready explanation. In the case of H as a substituent there are two sites for hydrogen bonding to the electron-deficient transition-state oxygen atom, instead of one, as in all the other transition states. Bascombe and Bell have pointed out the importance of such hydrogen bonding.[20] With the acetyl group as a substituent, protonation can occur on the carbonyl oxygen, followed by the loss of acetic acid as a leaving group. This path is not generally open to other substituents.

These results do not, in any sense, prove the operation of the three effects listed. One could, probably, find other satisfactory explanations for them. Nevertheless, these postulates provide a self-consistent picture and are also consistent with our earlier conclusions about the mechanism of this reaction.

The previous report[5] of insensitivity of hydrochloric acid induced deoxymercuration to the structure of the alkoxyl group may have been due to compensations among the various effects, coupled with an unfortunate, and limited, selection of substituents.

TABLE II

ANALYSES AND MELTING POINTS FOR $ROCH_2CH_2HgI$

No.[a]	C, % Calcd.	C, % Found[b]	H, % Calcd.	H, % Found[b]	M.p., °C.
1	16.80	16.71	3.03	3.22	80.0–80.5
3	16.80	17.03	3.03	3.10	54.5–55.0
4	14.48	14.63	2.65	2.78	80.6–81.2
5	15.74	15.66	2.40	2.45	108–110[c]
6	16.80	16.62	3.03	2.91	54.5–55.0
7	16.80	17.02	3.03	3.17	44.5–45.0
8	11.97	11.99	2.14	2.25	50.0–50.5
9	11.51	11.37	2.16	2.43	63.0–63.5
11	13.94	14.15	2.56	2.56	50.0–50.5
12	16.27	16.47	2.49	2.66	*d*
13	25.18	25.00	2.73	2.79	40.0–40.5
15	14.10	14.23	1.88	1.95	46–50
16	10.56	10.54	1.32	1.52	150–151[c]

[a] Numbers from Table I. [b] Analyses were by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. [c] Melted with decomposition. [d] Uncrystallizable oil.

Experimental

Kinetic procedures and the preparation of solvents, acid, and base have been previously described.[7]

Oxymercurials were prepared by dissolving or suspending 20 g. of mercuric acetate (J. T. Baker Chemical Co., analyzed reagent) in 100 ml. of the appropriate alcohol, and passing in as much gaseous ethylene as the mixture would take up. The alcohols were Distillation Products Industries, Eastman grade; Aldrich Chemical Co., research grade; or else were redistilled before use and shown to have suitable physical properties. The ethylene uptake generally required several hours. Magnetic stirring of the reaction mixture during the gas uptake often accelerated the uptake.

Further processing followed the procedure of Wright,[6] except that the products were taken up in chloroform and equilibrated three times with 10% aqueous sodium iodide to free them of mercuric iodide.

All the products had suitable infrared spectra, including one which was an uncrystallizable oil. Table II gives the analytical data and melting points for all compounds which are previously unreported.

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[19] See ref. 10, p. 134.

[20] K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

Poisoning Effects and Steric Facilitation in Catalytic Hydrogenation of Perphenylated Group IVb Atoms

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Studies of the nickel-catalyzed, heterogeneous hydrogenation of tetraphenyl derivatives of silicon, germanium, tin, and lead have led to the observation that the sterically crowded silicon compound absorbs hydrogen readily to give tetracyclohexylsilane while the others do not react under equivalent conditions. Even the less hindered silicon homolog, triphenylsilane, is not particularly reactive. It was observed that the presence of any of these other phenyl derivatives during hydrogenation of tetraphenylsilane affected the reaction seriously. Triphenylsilane and tetraphenylgermane markedly slowed hydrogen uptake, while the tin and lead analogs prevent any uptake. These results are interpreted as indicative of a poisoning effect on the catalyst by coordination with the central atom. Where initial steric hindrance prevents such coordination, normal hydrogenation of the phenyl groups occurs.

Relatively little work has been described on the hydrogenation of the tetraphenyl compounds of group IV elements other than carbon. Ipatiev and Dolgov[1] found no evidence of hydrogenation when tetraphenylsilane was treated with hydrogen at high temperature and pressure in the absence of catalyst. Recently, however, tetraphenylsilane was reported to undergo hydrogenation with difficulty in the presence of a W-6 Raney nickel catalyst[2] to produce tetracyclohexylsilane.[3]

It has been found in this laboratory that tetraphenylsilane is readily hydrogenated to tetracyclohexylsilane, in high yield (90%), by means of a commercial nickel catalyst (Girdler G 49-A). Of interest, initially, was

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[1] V. N. Ipatiev and B. N. Dolgov, *Ber.*, **62**, 1220 (1929).

[2] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

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