Chemistry

Academician A. N. NESMEYANOV, A. E. BORISOV, I. S. SAVEL' EVA

1964

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. N. NESMEYANOV, A. E. BORISOV, I. S. SAVEL' EVA

KINETICS OF THE ACIDOLYSIS OF SYMMETRICAL AROMATIC AND ALIPHATIC MERCURY COMPOUNDS

A series of studies has been devoted to the acidolysis of complete organomercury compounds from the point of view of establishing the relationship of this reaction to the nucleophilicity of the radical, both qualitatively and quantitatively,

$$R_2Hg + HX \rightarrow RHgX + RH$$

([1–9]).

Recently we briefly described the results of studying the kinetics of the acidolysis of several symmetrical organomercury compounds ([10,11]), and the continuation of research in this area of chemistry enables us to describe new results of our observations. We carried out the acidolysis in 90% aqueous dioxane. The reaction rate was determined acidimetrically. The amount of reacted R_2Hg, calculated on the basis of acidimetry, corresponded (with a discrepancy of no more than 6%) to the amount of isolated reaction products. This was verified by us using the examples of the decomposition of di-*p*-tolylmercury, di-*p*- and di-*o*-anisylmercury. All the reactions we investigated are of second order. Table 1 gives the values of the rate constants for the acidolysis of R_2Hg, arranged in order of decreasing magnitude, and the parameters of the Arrhenius equation.

Diphenyl- and divinylmercury react at approximately the same rate, as follows from comparison of the values of the reaction rate constants; therefore, in discussing the experimental results we shall compare their reactivity with the reactivity of other organomercury compounds.

Introduction of alkoxy substituents into the *o*- and *p*-positions and alkyl substituents into the *o*-, *p*- and *m*-positions of the benzene ring, as well as introduction of methyl and phenyl substituents into the β-position of the vinyl group, leads to an increase in the rate of the acidolysis reaction. This is an obvious consequence of the electron-donating properties exhibited by the indicated substituents, which lead to an increase in the nucleophilicity of the carbon bound to mercury, i.e., to a greater electronegativity of the radical according to Kharasch.

The reaction rate, as a function of the position of the methoxy group in the benzene ring, decreases in the series p-$CH_3O \gg o$-$CH_3O > C_6H_5 > m$-CH_3O. The considerable decrease in rate under the influence of the o-methoxy group in comparison with the p-isomer is possibly connected with the ortho effect. The retarding effect of methoxyl in the meta position is an obvious consequence of the $-I$-effect of this group in the absence of a $+T$-effect. The influence of the methyl group on the rate of acidolysis, depending on its position in the benzene ring, decreases in the series o-$CH_3 > p$-$CH_3 > m$-CH_3. The reactivity increases slightly on going from the p-methyl group to p-ethyl. Accumulation of methyl groups in the o- and p-positions causes acceleration of the reaction; thus dimesitylmercury has the largest rate constant for the decomposition reaction among the aromatic compounds considered.

Aromatic compounds containing halides in the o-, p- and m-positions of the benzene ring, acetoxy and carbomethoxy groups in the o- and p-positions, a methoxy group in the m-position, and β-chlorovinyl compounds react more slowly than diphenyl- and divinylmercury. Thus, halides in the o-, p- and m-positions, as usual, passivate the benzene ring with respect to electrophilic attack. The situation is similar with a halide in the β-position of the vinyl group. For p-halogen-substituted compounds, the rate of re-

Table 1

No.	R	Rate constants k, $l \cdot sec^{-1} \cdot mol^{-1}$, at the corresponding temperatures (°C)	E, cal/mol	$\lg pz_0$
1	$1,3,5$-$(CH_3)_3C_6H_2$	$3.65 \cdot 10^{-1}$ [a] (20)		
2	trans-$CH_3CH{=}CH$–	$8.84 \cdot 10^{-2}$ (11); $1.34 \cdot 10^{-2}$ (15); $2.13 \cdot 10^{-1}$ (20)	16100	11.351
3	n-$C_2H_5OC_6H_4$–	$1.78 \cdot 10^{-1}$ (20); $6.63 \cdot 10^{-1}$ [b] (30)		

No.	R	Rate constants k, $l \cdot sec^{-1} \cdot mol^{-1}$, at the corresponding temperatures (°C)	E, cal/mol	$\lg pz_0$
4	cis-$CH_3CH{=}CH-$	$6.62 \cdot 10^{-2}$ (11); $1.03 \cdot 10^{-1}$ (15); $1.66 \cdot 10^{-1}$ (20)	16400	11.473
5	*n*-$CH_3OC_6H_4-$	$1.25 \cdot 10^{-1}$ (20); $5.34 \cdot 10^{-1}$ [b] (30)		
6	$C_6H_5CH{=}CH-$	$9.48 \cdot 10^{-2}$ (20)		
7	trans-$CH_3C(CH_3OC(O))=CCH_3-$	$5.40 \cdot 10^{-2}$ (20)		
8	cis-$CH_3C(CH_3OC(O))=CCH_3-$	$4.32 \cdot 10^{-2}$ (20)		
9	α-C_4H_3S α-thienyl	$3.42 \cdot 10^{-2}$ (20); $1.16 \cdot 10^{-1}$ (30)		
10	*o*-$CH_3C_6H_4-$	$4.73 \cdot 10^{-2}$ (30)		
11	*n*-$C_2H_5C_6H_4-$	$4.26 \cdot 10^{-2}$ (30)		
12	*n*-$CH_3C_6H_4-$	$1.00 \cdot 10^{-2}$ (20); $4.14 \cdot 10^{-2}$ (30); $1.44 \cdot 10^{-1}$ (40)	24300	15.165

No.	R	Rate constants k, $l \cdot sec^{-1} \cdot mol^{-1}$, at the corresponding temperatures (°C)	E, cal/mol	$\lg pz_0$
13	cis-$C_6H_5CH{=}CC_6H_5$—	$2.12 \cdot 10^{-3}$ (20); $6.94 \cdot 10^{-3}$ (30); $2.48 \cdot 10^{-2}$ (40); $1.41 \cdot 10^{-1}$ [c)]	22100	14.346
14	*o*-$CH_3OC_6H_4$—	$3.82 \cdot 10^{-3}$ (20); $1.42 \cdot 10^{-2}$ (30); $4.95 \cdot 10^{-2}$ (40)	23350	15.018
15	α-$C_{10}H_7$—α-naphthyl	$1.28 \cdot 10^{-2}$ (30); $5.10 \cdot 10^{-2}$ (40); $1.63 \cdot 10^{-1}$ (50)	24650	15.915
16	*m*-$CH_3C_6H_4$—	$1.28 \cdot 10^{-2}$ (30)		
17	$CH_2{=}CH$—	$2.77 \cdot 10^{-3}$ (20); $3.87 \cdot 10^{-3}$ (30); $2.33 \cdot 10^{-2}$ (40)	19400	11.930
18	C_6H_5—	$1.77 \cdot 10^{-3}$ (20); $6.65 \cdot 10^{-3}$ (30); $2.36 \cdot 10^{-2}$ (40)	23600	14.866

No.	R	Rate constants k, $l \cdot sec^{-1} \cdot mol^{-1}$, at the corresponding temperatures (°C)	E, cal/mol	$\lg pz_0$
19	*n*-FC_6H_4—	$5.82 \cdot 10^{-3}$ (30); $2.21 \cdot 10^{-2}$ (40); $7.64 \cdot 10^{-2}$ (50)	25000	15.819
20	*m*-$CH_3OC_6H_4$—	$5.52 \cdot 10^{-3}$ (30); $5.78 \cdot 10^{-2}$ (50); $1.75 \cdot 10^{-1}$ (60)	23000	14.343
21	trans-$C_6H_5CH{=}CC_6H_5$—	$1.29 \cdot 10^{-2}$ (30); $4.18 \cdot 10^{-2}$ (50); $1.36 \cdot 10^{-1}$ (60)	24400	15.168
22	*n*-ClC_6H_4—	$1.23 \cdot 10^{-3}$ (30); $1.42 \cdot 10^{-2}$ (50); $4.64 \cdot 10^{-2}$ (60)	24550	14.906
23	*n*-BrC_6H_4—	$8.46 \cdot 10^{-4}$ (30); $3.16 \cdot 10^{-3}$ (40); $3.65 \cdot 10^{-2}$ (60)	25200	15.126

[d)] [c)]

No.	R	Rate constants k, $l \cdot sec^{-1} \cdot mol^{-1}$, at the corresponding temperatures (°C)	E, cal/mol	$\lg pz_0$
24	*m*-FC_6H_4—[d]	($2.56 \cdot 10^{-4}$) (30); $4.17 \cdot 10^{-3}$ (50); $1.36 \cdot 10^{-2}$ (60); $4.78 \cdot 10^{-2}$ (70)	26800	15.762
25	*m*-ClC_6H_4—	($2.09 \cdot 10^{-4}$) (30); $3.15 \cdot 10^{-3}$ (50); $1.14 \cdot 10^{-2}$ (60); $3.56 \cdot 10^{-2}$ (70)	26700	15.601
26	$C_6H_5C(CH_3OCOC_6H_5)=CC_6H_5$	2.80 · 10^{-2} (70)		
27	*o*-$CH_3OCOC_6H_4$—	$2.75 \cdot 10^{-3}$ (70)		
28	trans-ClCH=CH—	$1.00 \cdot 10^{-2}$ (60); $2.56 \cdot 10^{-2}$ (70); $6.54 \cdot 10^{-2}$ (80)	21950	12.411
29	C_2H_5—	$1.95 \cdot 10^{-3}$ (50); $7.52 \cdot 10^{-3}$ (60); $2.57 \cdot 10^{-2}$ (70)	28400	16.538
30	*n*-$CH_3OOCC_6H_4$—	($1.06 \cdot 10^{-4}$) (30); $2.48 \cdot 10^{-2}$ (70)		

No.	R	Rate constants k, $l \cdot sec^{-1} \cdot mol^{-1}$, at the corresponding temperatures (°C)	E, cal/mol	$\lg pz_0$
31	cis-ClCH=CH—	$5.14 \cdot 10^{-3}$ (60); $1.38 \cdot 10^{-2}$ (70); $3.53 \cdot 10^{-2}$ (80)	22500	12.493
32	*o*-$CH_3OOCC_6H_4$—	$1.36 \cdot 10^{-2}$ (70)[e]		
33	*n*-C_4H_9—	$1.18 \cdot 10^{-2}$ (70)		
34	*o*-ClC_6H_4—	$1.84 \cdot 10^{-3}$ (60)		
35	$C_6H_5CH_2$—	Immeasurably small (60); $3.54 \cdot 10^{-3}$ (70)		

$[R_2Hg] \simeq 0.005$ mol/l, $[HCl] \simeq 0.01$ mol/l.
a) $[HCl] \simeq 0.005$ mol/l. $[R_2Hg] \simeq 0.0025$ mol/l.
b) $[HCl] \simeq 0.006$ mol/l; c) $[R_2Hg] \simeq 0.00068$ mol/l. Obtained as a diastereomer, m.p. 165–166°. The position in the series of trans-mercurybisstilbenes (No. 21) should be regarded as provisional, in view of the excessively low concentration of this compound in solution and the incomparability of the data obtained in this case.
d) Obtained from *m*-FC_6H_4MgBr and $HgBr_2$, m.p. 117–119°. The values of k in parentheses were obtained by extrapolation.
e) Obtained from *o*-$CH_3OOCC_6H_4HgCl$ and $Sn(ONa)_2$, m.p. 132–133°. The remaining mercury-organic compounds were obtained in accordance with literature data.

The reaction rate decreases in the series *n*-FC_6H_4 > *n*-ClC_6H_4 > *n*-BrC_6H_4. The same regularity is also observed in the case of the *m*-halogen-substituted compounds on going from fluorine to chlorine. Depending on the position of chlorine in the benzene ring, the reaction rate decreases in the series *n*-ClC_6H_4 > *m*-ClC_6H_4 ≫ *o*-ClC_6H_4. For the *n*- and *m*-fluorine-substituted compounds, *n*-FC_6H_4 > *m*-FC_6H_4, the same order of reactivity is retained. Acetoxy and carbomethoxy groups in the *o*- and *n*-positions are electron acceptors, causing

Fig. 1 and Fig. 2: plots of $\lg k$ against substituent constants

Figure 1: Fig. 1 and Fig. 2: plots of $\lg k$ against substituent constants

a decrease in the electron density at the carbon atom bonded to mercury.

The rate of reaction of diallylmercury with hydrochloric acid is so high that it cannot be measured.

Contrary to the opinion of Dessy and Kim [7] on the incompatibility of the results of acidolysis of symmetrical and unsymmetrical organomercury compounds, the data obtained by us on the reactivity of symmetrical compounds for the most part (except di-*o*-anisylmercury, di-*p*-fluorophenylmercury, di-*o*-chlorophenylmercury, and di-α-naphthylmercury) coincide with the electronegativity series of Kharasch.

Fig. 1. Dependence of $\lg k$ on Hammett σ, $\lg k$ on $\frac{\sigma+\sigma^+}{2}$, $\lg k$ on σ_m^0, and $\lg k$ on σ^*

Fig. 2. Dependence of $\lg k/k_0$ on σ_π^+

For the acidolysis of *m*- and *p*-substituted organomercury compounds, a linear dependence of $\lg k$ on Hammett σ^*, σ^+, and $\frac{\sigma+\sigma^+}{2}$ was observed. The best correlation is observed when $\frac{\sigma+\sigma^+}{2}$ is used (Fig. 1). Such a correlation of the acidolysis constants of organomercury compounds was also noted and interpreted by Dessy [8].

Thus, although the attack of HCl on an organomercury compound proceeds, in general, similarly to electrophilic substitutions in an aromatic ring (correlation with σ^+), nevertheless it deviates somewhat (toward correlation with σ). Whether the causes of this deviation lie in the action of the Cl^- anion or in the influence of the second group attached to mercury remains to be clarified.

For the acidolysis of *m*-substituted organomercury compounds $(m\text{-}RC_6H_4)_2Hg$, where R = CH_3, CH_3O, H, F, and Cl, a correlation of $\lg k$

* According to McDaniel and Brown [12].

from σ^0 (15) with $r = 0.996$ at $\rho = -4.13$ (Fig. 1); correlation of $\lg k$ for the acidolysis of these same compounds with σ_m^* gives poorer results, with $r = 0.978$ and $\rho = -4.19$.

In the investigation of unsaturated organomercury compounds of the type $(R—CH{=}CH)_2Hg$, it was established that for di-*trans*-propenylmercury (R = CH_3), di-ω-styrylmercury (R = C_6H_5), divinylmercury (R = H), and di-*trans*-β-chlorovinylmercury (R = Cl), the Taft equation is applicable with the polar constants

Table 2

Nos. of compounds in Table 1	σ	r	ρ
3, 5, 11, 12, 16, 18, 19, 20,22-25, 30*	σ_π and $\sigma_M^{(12)}$	0.977	−4.92
3, 5, 11, 12, 16, 18, 19, 20,22-25, 30*	$\sigma^{+(13,14)}$	0.984	−3.07
5, 11, 12, 16, 18, 19, 20,22-25, 30	$(\sigma + \sigma^+)/2$	0.996	−3.78

* The values of σ were taken as for the $COOC_2H_5$ group.

of substituents σ^* (16,17) (for the entire radical bound to mercury), with $r = 0.996$ and $\rho = -6.07$ (Fig. 1). A correlation is also observed for $\lg k/k_0$ with Hammett σ_p, σ_π^+, and $(\sigma + \sigma_\pi^+)/2$ (Fig. 2), this time for the substituents R of these unsaturated organomercury compounds; the best correlation is attained when σ_π^+ is used, with $r = 0.972$ and $\rho = -7.60$. This probably indicates a greater conjugation of the β-substituents of the unsaturated system with the reaction center as compared with the aromatic system, and also indicates that C=C, like the benzene nucleus in the case of the action of para-substituents, plays the role of a conducting system; moreover, the constants $\rho = -7.60$ at 30°** (18) for the C=C system are, in absolute value, 2.5 times higher than for the benzene system.

The trans isomers of the unsaturated organomercury compounds we investigated, except for ω-mercuribisstilbene, have a larger rate constant than the corresponding cis compounds. These data agree with the greater reactivity of the trans isomers previously observed by two of us (19-22).

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
29 XII 1963

CITED LITERATURE

1. M. S. Kharasch et al., J. Am. Chem. Soc., **47**, 1948 (1925); **48**, 3130 (1926); **54**, 674 (1932); J. Org. Chem., **3**, 347 (1938); **3**, 405 (1938); **3**, 409 (1938).

2. F. C. Whitmore, H. Bernstein, J. Am. Chem. Soc., **60**, 2626 (1938).

3. A. H. Corwin, M. A. Naylor, J. Am. Chem. Soc., **69**, 1004 (1947).

4. F. Kaufman, A. H. Corwin, J. Am. Chem. Soc., **77**, 6280 (1955).

5. S. Winstein, T. I. Taylor, J. Am. Chem. Soc., **77**, 3747 (1955).

6. F. Nerdel, S. Makover, Naturwiss., **20**, 490 (1958).

7. R. E. Dessy, G. F. Reynolds, J. Y. Kim, J. Am. Chem. Soc., **81**, 2683 (1959).

8. R. E. Dessy, J. Y. Kim, J. Am. Chem. Soc., **82**, 686 (1960); **83**, 1167 (1961).

9. O. A. Reutov, I. P. Beletskaya, M. Ya. Aleynikov, ZhOKh, **36**, 489 (1962).

10. A. N. Nesmeyanov, A. E. Borisov et al., Izv. AN SSSR, OKhN, 1961, 726.

11. A. N. Nesmeyanov, A. E. Borisov, I. S. Savel' eva, Izv. AN SSSR, OKhN, 1961, 2241.

12. D. H. McDaniel, H. C. Brown, J. Org. Chem., **23**, 420 (1958).

13. H. C. Brown, J. Okamoto, J. Am. Chem. Soc., **80**, 4979 (1958).

14. J. Okamoto, T. Ihukai, H. C. Brown, J. Am. Chem. Soc., **80**, 4969 (1958).

15. R. W. Taft, Jr., J. Phys. Chem., **64**, 1805 (1960).

16. R. W. Taft, Steric Effects in Organic Chemistry, Chap. XIII, Inostrannaya literatura, 1960.

17. J. Hine, W. C. Bailey, J. Am. Chem. Soc., **81**, 2075 (1959).

18. L. P. Hammett, J. Am. Chem. Soc., **59**, 96 (1937).

19. A. N. Nesmeyanov, A. E. Borisov, R. I. Shepeleva, Izv. AN SSSR, OKhN, 1949, 582.

20. A. E. Borisov, Candidate' s Dissertation, 1952.

21. A. E. Borisov, Izv. AN SSSR, OKhN, 1961, No. 6, 1036.

22. A. E. Borisov, V. D. Vil' chevskaya, A. N. Nesmeyanov, Izv. AN SSSR, OKhN, 1954, 1011.

* According to McDaniel and Brown (12).
** Calculated according to Hammett (18).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.