[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOUISIANA POLYTECHNIC INSTITUTE]

The Reactions of Alkyl Halides with Carboxylic Acids. I. Kinetic Studies in Acetic Acid and Nitromethane

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The reaction of *t*-butyl chloride with acetic, formic and chloroacetic acids has been studied kinetically in solutions of both acetic acid and nitromethane. The reaction with formic acid is second order in added acid in both solvents and the same seems to be true of acetic and chloroacetic acids. The reactions in acetic acid are believed to involve both electrophilic and nucleophilic activity by the added acid. Some support for this view is found in a mutual rate enforcement by the formic and chloroacetic acids and cryoscopic evidence that the two added acids were not dimerized with themselves in acetic acid. The reactions in nitromethane are less clearly interpreted since there is a possibility that acid dimers are serving as electrophiles to aid carbonium ion formation.

In a study designed to measure the relative reactivity of carboxylic acids toward an alkyl halide, we chose *t*-butyl chloride as a typical compound sensitive to electrophilic catalysis.[1,2] Acetic, formic and chloroacetic acids were chosen because of the large amount of previous work done with the first two[2-4] and the increasing acid strength of the three in the order listed.

Experimental

All reagents were tested for purity and purified where necessary. The kinetic measurements were made using a specially constructed flask which permitted total immersion of the reaction mixture. Samples were taken at appropriate intervals, and the excess sodium salt of the acid present was titrated with perchloric acid in acetic acid according to Winstein.[5] The *t*-butyl chloride and sodium salt concentrations were about 0.1 M each in all runs. Infinite time titers were taken for most runs and the pseudo first-order rate constants were calculated from plots of % remaining chloride against time and the change in concentration for a fixed period of time against time. The results usually agreed to at least ±5% or better. The rates with chloroacetic acid were less reproducible. Initial rates were used for the reactions using 1–2 M added acid. The temperatures quoted may be in error by 0.1°. The results are given in Tables I and III. First and second-order rate constants are calculated and given also.

TABLE I

THE SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN ACETIC ACID SOLUTIONS AT 49.8°

Added acid	C, mole/l.	k obsd[a]	k[b]	k/c	k/c^2
None	...	0.69 ± 0.02	...	...	...
Formic	1.0	1.4 ± .2	0.70	0.70	0.70
Formic	2.0	2.56 ± .03	1.87	0.93	.47
Formic	3.0	4.8 ± .1	4.1	1.4	.46
Formic	4.0	8.5 ± .4	7.8	1.9	.49
Chloroacetic	2.0	1.8 ± .1	1.1	0.55	.28
Chloroacetic	3.0	3.1 ± .2	2.4	0.80	.27
Chloroacetic and formic	2.0 each	6.0 ± .1[c]	...	...	...

[a] All rate constants are × 10^{-5} sec.$^{-1}$. [b] k_{obsd} minus the rate at zero added acid concentration. [c] Calculated value 4.3 ± 0.1.

Discussion

We were rather surprised to find that there was little evidence for mutual interaction between acetic acid and the other two acids in acetic acid solution. The rates were proportional to the square of the formic acid concentrations (and probably so for the chloroacetic acid concentrations), indicating that either these two acids were serving as *both* the *nucleophile* and the *electrophile in acetic acid* or that a dimer was serving as the electrophile. The latter seems unlikely in acetic acid solution especially since the intercepts at zero concentration as shown in Fig. 1 compare favorably with the observed rate in acetic acid alone.

As a simple test to determine the state of formic and chloroacetic acid in acetic acid and possibly in nitromethane, some freezing point depression data were taken. These experiments were designed to determine roughly the degree of association, and the results in Table II are expressed in terms of calculated molal freezing point depression constants.

TABLE II

FREEZING POINT DEPRESSION DATA

Solvent	Solute	Molality	Δt	K[a]
CH_3COOH	HCOOH	1.3	4.3	3.30
CH_3COOH	HCOOH	2.6	8.7	3.34
CH_3COOH	HCOOH	3.9	12.8	3.26
CH_3COOH	HCOOH	1.27	4.2	3.30
CH_3COOH	HCOOH	1.27	4.17	3.29
CH_3COOH	HCOOH and $ClCH_2COOH$	1.27 and 0.54	5.94	3.28
CH_3COOH	$(CH_3)_2CHOH$	0.63	2.1	3.34
CH_3COOH	$(CH_3)_2CO$	0.65	2.3	3.54
$C_6H_5NO_2$	HCOOH	1.1	3.4	3.1
$C_6H_5NO_2$	$(CH_3)_2CO$	0.565	3.7	6.5
p-$CH_3C_6H_4NO_2$	HCOOH	1.31	5.18	3.95
CH_3COOH	$(CH_2COOCH_3)_2$[b]	3.6	11.2	3.12
CH_3COOH	$(CH_2COOCH_3)_2$[b]	1.1	3.7	3.36

[a] Literature values of K for acetic acid, nitrobenzene and *p*-nitrotoluene are 3.9, 6.8 and 7.8, respectively. [b] James Kendall and J. E. Booge, THIS JOURNAL, **38**, 1712 (1916).

The solute concentrations were purposely made large to permit direct comparison with our kinetic runs and this may be the factor responsible for the lower average value of K (3.3) for acetic acid as compared to 3.9. These figures lead to the conclusion that none of the solutes were appreciably dimerized in acetic acid at its freezing point. Baud[6] also studied the formic acid—acetic acid system and reached the same conclusion.

In order to evaluate the acids independently, nitromethane solutions were used. These data are given in Table III.

In nitromethane it is evident that the reaction is second-order in formic acid and probably the same for acetic and chloroacetic acids. It is realized

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[1] E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

[2] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

[3] S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

[4] L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 945 (1940).

[5] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

[6] M. E. Baud, *Bull. Soc. Chim.*, **13**, 435 (1913).

TABLE III

THE SOLVOLYSIS TO *t*-BUTYL CHLORIDE IN NITROMETHANE SOLUTIONS OF ACETIC, CHLOROACETIC AND FORMIC ACIDS at 50.0°

Acid	*C*, mole/l.	*k*, obsd.[a]	*k*[b]	k/c	k/c^2
Acetic	2.0	0.73 ± 0.01	0.20	0.10	0.050
Acetic	4.0	1.31 ± .02	0.78	0.19	0.049
Chloroacetic	0.97	2.2 ± .1	1.6	1.7	1.7
Chloroacetic	1.97	6.1 ± .1	5.5	2.8	1.4
Chloroacetic	2.97	13.5 + .3	12.9	4.3	1.5
Formic	1.4	4.88 ± .02	3.88	2.78	1.98
Formic	2.5	13.3 ± .1	12.3	4.92	1.97
Formic	3.0	18.9 ± .1	17.9	5.96	1.99
Formic	3.5	25.6 ± .2	24.6	6.75	1.93
Formic	4.0	32.1 ± .2	31.1	7.78	1.94
Formic and chloroacetic	2.0 and 1.97	27.6 ± .2[c]	...	...	...
Formic and acetic	2.0 and 2.0	9.7 ± .1[d]	...	...	...

[a] All rate constants are × 10^{-5}sec.$^{-1}$. [b] k_{obsd} minus the rate at zero added acid concentration. [c,d] Calculated values 16 ± 1 and 9.6 ± 0.1.

that the data for acetic acid are not adequate for establishing the kinetic order, but it should be pointed out that the position of the intercept on a second-order plot is more consistant with the values for the other acids. There is good evidence for mutual interaction for formic and chloroacetic acids in both acetic acid and nitromethane solvents but acetic acid does not show mutual interaction in either solvent. Thus it appears that formic and chloroacetic acids are both more nucleophilic and more electrophilic than acetic acid. The similarity of formic and chloroacetic acids is probably due to a greater electrophilic contribution by chloroacetic acid coupled with a greater nucleophilic contribution by formic acid.

The possibility that a dimer of the acids is serving as an electrophile in nitromethane solutions requires careful consideration. The non-existence of acid dimers in nitromethane could not be so readily demonstrated by the method used for acetic acid solutions. Using nitrobenzene and 4-nitrotoluene as solvents it was found that cryoscopic data (Table II) indicated complete dimerization of formic acid even at the higher melting point of 4-nitrotoluene (51°). The uncertainty of extrapolating from these solvents to nitromethane made it desirable to use some other approach so a careful study of the infrared absorption bands of formic acid in the 3 and 6 μ regions was made. Both bands are known to shift to longer wave lengths upon dimerization.[7] The absorption bands in these regions were very strong, and it may be that the exact positions observed are the results of bands for both the monomers and dimers of formic acid.

TABLE IV

INFRARED SPECTRA OF FORMIC ACID IN NITROMETHANE SOLUTIONS

C, moles/l.	3μ	6μ	*C*, moles/l.	3μ	6μ
10.0	3.20	5.9	2.0	2.94	5.79
5.0	3.11	5.89	1.25	2.93	5.79
4.0	3.11	5.87	0.2	2.9	5.74
2.5	2.93	5.80			

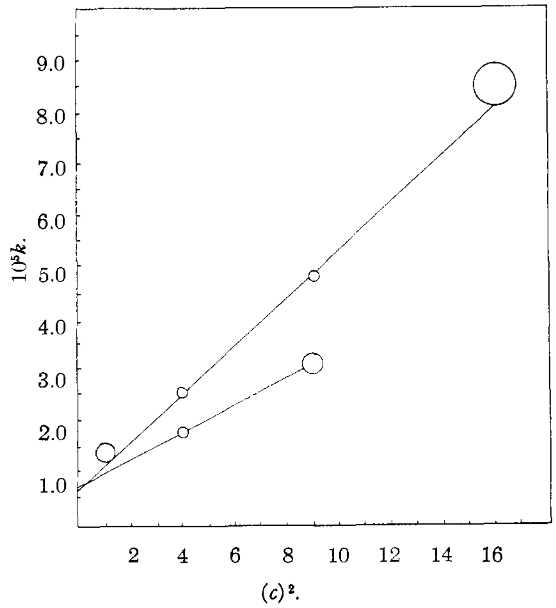

Fig. 1.—The solvolysis of *t*-butyl chloride in acetic acid solutions at 49.8°: I, HCOOH solutions; II, $ClCH_2$–COOH solutions.

The results given in Table IV are taken to mean that formic acid is not completely dimerized in nitromethane at concentrations below 10 *M*. If appreciable amounts of acid monomer are present, then we can reasonably assume that the monomer rather than the dimer is the reactive species. Such an assumption is consistent with the infrared spectral data and the results of our studies using acetic acid solutions.

The question of products should be discussed briefly. The view that the nucleophile would determine the products is not necessarily correct. A solvent molecule could easily aid ionization of a halide to form a solvated carbonium ion which, depending on its stability, could exchange solvating molecules, become symmetrically solvated and eventually react to form the thermodynamically stable product. The increasing racemization with increasing acetone content in the hydrolysis of α-phenylethyl chloride to α-phenylethanol[8] can be accounted for by the above explanation. In view of the possibilities just discussed it was not considered necessary to undertake product analysis at this time.

The third-order kinetics observed and the mutual interaction of the two acids are similar to the observations of Swain[9] for the reaction of triphenylmethyl chloride and methyl bromide with methanol and phenol in benzene solution. Our conclusion that *t*-butyl chloride is sensitive to nucleophilic as well as electrophilic attack in solvolytic reactions is also in agreement with Swain[10] and Tommila[11] but not with Winstein[2,3] or the earlier

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[7] M. M. Davies, *J. Chem. Phys.*, **16**, 267, 274 (1948); M. M. Davies and G. B. B. M. Sutherland, *ibid.*, **6**, 755 (1938).

[8] E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1208 (1937).

[9] C. G. Swain, THIS JOURNAL, **70**, 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948).

[10] C. G. Swain and R. B. Mosely, *ibid.*, **77**, 3727 (1955).

[11] Eero Tommila, *Acta Chem. Scand.*, **9**, 975 (1955), and preceding papers.

views of Hughes and Ingold.[1,12] In a recent paper[13] they reported a study of nucleophilic displacements on *t*-butyl halides in Finkelstein's reaction but did not apply their observation to solvolysis reactions.

Our results differ from those of Gelles, Hughes and Ingold[1] who used water, phenol and methanol in nitromethane solution to react with *t*-butyl bromide. In the concentration ranges studied they found evidence for electrophilic catalysis only. The two highest concentrations of water used did show evidence of a higher order reaction, however. The only explanation that we can offer for this discrepancy is that the concentrations they used were so low that the reagents could not compete with either the solvent or added pyridine as the nucleophile. The reaction with pyridine alone was a significant part of the total rate even though it was not sensitive to pyridine concentration. The work of Hawthorne and Cram[14] indicates that a reaction of this type may not necessarily be very sensitive to the nucleophile.

Further work is contemplated to determine the importance of gross dielectric constant, the entropy effect and variations in the substrate and products.

Acknowledgments.—The authors wish to express their appreciation to E. S. Lewis and M. F. Hawthorne for their constructive criticism and helpful suggestions.

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 308–418.

(13) P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, *J. Chem. Soc.*, 3200 (1955).

(14) M. F. Hawthorne and D. J. Cram, THIS JOURNAL, **76**, 3451, (1954).

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[CONTRIBUTIONS FROM SINCLAIR RESEARCH LABORATORIES, INC.]

t-Butylation of Aromatics with Isoamylene[1]

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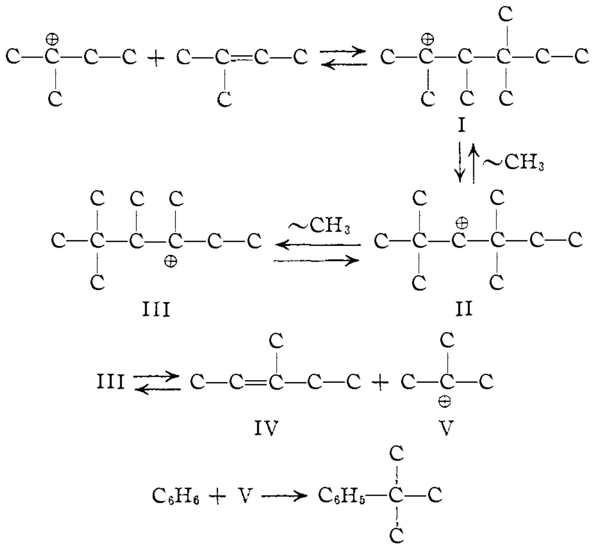
It has been found that *t*-butyl derivatives are frequently produced, often in yields up to 25%, during the reaction of aromatics with isoamylene. The C_4-fragment probably arises from the dimerization of the C_5-olefin followed by rearrangement and scission of the resulting C_{10}-olefin to yield C_4- and C_6-fragments. Conditions which favor this reaction are described.

During the course of an investigation of the alkylation of benzene with isoamylene[3] it was noted that under certain conditions *t*-butylbenzene is formed as one of the important products of reaction.

It is proposed that *t*-butylbenzene is formed by the mechanism



The first-formed *t*-amyl cation reacts with a molecule of olefin to form a decyl cation I which by a series of methyl shifts forms the tertiary carbonium ion III. If one prefers not to envision the formation of a secondary carbonium ion from a tertiary (*e.g.*, II from I), one can postulate a 1,3-methyl shift to form III directly. Cation III then decomposes by β-scission to form a hexene, IV, and the *t*-butyl cation, V. The cation V reacts with a molecule of benzene to form *t*-butylbenzene.

The following evidence can be presented for this mechanism. When benzene was allowed to react with 2-methyl-2-butene in the presence of a small amount of aluminum chloride which was added gradually during the course of the reaction, *t*-butylbenzene was formed in 25% yield. An 11% yield of pentylbenzene also was formed. Spectrometric analysis of the higher boiling products indicated the presence of both hexylbenzene (probably derived from IV) and decylbenzene (reaction of benzene with I, II or III). Disubstitution was essentially absent. When the dimer of 2-methyl-2-butene (formed in the presence of sulfuric acid) was used to alkylate benzene (aluminum chloride catalyst), a 17% yield of *t*-butylbenzene was formed as well as 39% of pentylbenzene.

The formation of several of the intermediate cations mentioned in the above mechanism is amply documented. The action of sulfuric acid on methylisopropylcarbinol has been shown[4,5] to yield 3,4,5,5-tetramethyl-2-hexene (which corresponds to cation III). Whitmore and Mosher[4] obtained 45% of this decene and in addition 3% of 3-methyl-2-pentene (IV above) and 1% of diisobutylene (easily yields cation V). These authors state,

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(1) Presented in part at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955.

(2) Armour Research Foundation, Illinois Institute of Technology, Chicago, Ill.

(3) B. S. Friedman and F. L. Morritz, THIS JOURNAL, **78**, 2000 (1956).

(4) F. C. Whitmore and W. A. Mosher, *ibid.*, **63**, 1120 (1941).

(5) N. L. Drake, G. M. Kline and W. G. Rose, *ibid.*, **56**, 2076 (1934).