120–121° (5 mm.), n^{22}_{D} 1.4492 (lit.[7] b. p. 137–138° (12 mm.), n_{D} 1.4540). *Anal.* Calcd. for $C_{14}H_{27}OCl$: C, 68.09; H, 11.03; Cl, 14.4. Found: C, 68.50; H, 11.28; Cl, 14.5.

5-Butylnonene-4.[8]—A mixture of 50 g. (0.20 mole) of tributylacetyl chloride and 20 g. (0.223 mole) of dry cuprous cyanide[9] was refluxed for eight hours by means of a metal-bath at 220–240°. The apparatus was arranged for vacuum distillation and at 20 mm. a colorless oil distilled. The distillation was continued until the bath temperature reached 300°. The distillate was redistilled *in vacuo;* yield 29 g. (81%), b. p. 74–75° (3.5 mm.), n^{26}_{D} 1.4369 (lit.[4] b. p. 60° (1.2 mm.), n^{20}_{D} 1.4392). *Anal.* Calcd. for $C_{13}H_{26}$: C, 85.62; H, 14.38. Found: C, 85.84; H, 14.41. A similar experiment conducted at 100° for eight hours resulted in the recovery of the acid chloride.

5-Butylnonane.—A mixture of 22 g. of 5-butylnonene-4, 350 ml. of methanol and 5 g. of Raney nickel catalyst was reduced with hydrogen at 70° for 12 hours at a pressure of 1000 lb. p.s.i. The catalyst was removed by filtration, the methanol distilled *in vacuo* and the residual oil distilled; yield 12 g. (53%), b. p. 75–78° (3.5 mm.), n^{27}_{D} 1.4245, colorless oil (lit.[5] b. p. 217.5–218.5°, n^{19}_{D} 1.4273). *Anal.* Calcd. for $C_{13}H_{28}$: C, 84.69; H, 15.32. Found: C, 84.88; H, 15.25. 5-Butylnonene-4 was also reduced with Raney nickel and hydrogen in a Parr shaker at room temperature at a pressure of 50 lb. p.s.i.

Trimethylacetyl Cyanide.—A mixture of 96 g. (0.80 mole) of trimethylacetyl chloride and 76 g. (0.80 mole) of cuprous cyanide was refluxed for 20 hours. Upon distillation, a colorless liquid was obtained; yield 77.5 g. (87%), b. p. 120–122°, n^{27}_{D} 1.3940. *Anal.* Calcd. for C_6H_9ON: N, 12.61. Found: N, 12.21.

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(8) For comparison purposes an authentic sample of 5-butylnonene-4[4] was prepared by refluxing 100 g. of tributylcarbinol ("Org. Syn.," Coll. Vol. II, p. 603) and one gram of iodine for two hours; yield 76.7 g. (84%); b. p. 79–81° (4 mm.), n^{25}_{D} 1.4365.

(9) A sample of J. T. Baker C. P. Analyzed cuprous cyanide powder was dried overnight in an oven at 110°.

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Decomposition of the Isomeric Toluic Acids in the Ozonizer Discharge

BY CLARENCE N. STOVER, JR.,[1] AND WARREN M. GARRISON[2]

Bombardment of organic compounds with high energy radiation frequently results in the formation of complex mixtures of reaction products. With hydrocarbons, the types and relative amounts of products seem to indicate that bond rupture may occur at random in the molecule and that the probability of rupture of any particular type of bond is roughly proportional to its fractional concentration in the molecule.[3] With organic compounds containing polar groups, however, data have been obtained which suggest that selective bond rupture may also occur. For example, when organic acids are bombarded with alpha particles[4] or high energy deuterons,[5] one of the main reactions results in the formation of carbon dioxide and the paraffin hydrocarbon corresponding to the chain of the acid bombarded. With palmitic acid[6] at least 90% of all C–C bond ruptures seem to occur at the terminal COOH group.

TABLE I

COMPOSITION OF GASEOUS PRODUCTS IN VOLUME PER CENT.

	Meta		Ortho		Para	
H_2O	13.9	14.3	13.5	10.4	4.6	3.7
CO_2	31.6	31.2	26.9	27.8	16.5	15.7
H_2	10.1	9.8	13.5	15.0	21.2	33.3
CO	31.6	33.9	38.6	40.6	42.2	43.5
CH_4	0.0	0.0	0.0	0.0	3.7	2.8
Other[a] hydrocarbons	12.7	11.6	7.6	6.2	1.8	0.9

[a] Condensable in liquid air after removing water and carbon dioxide.

To obtain additional information on the radiation chemistry of organic acids, we have investigated the behavior of a series of isomeric acids in the ozonizer discharge which has been shown[7] to produce chemical effects similar to those occurring with high-energy radiation. The present paper reports the chemical effects produced by the ozonizer discharge on the toluic acids in the vapor state. The composition of the gaseous decomposition products is shown in Table I. The observed ratio of methane to carbon dioxide plus carbon monoxide is indicative of the relative number of C–CH_3 and C–COOH bond ruptures. With each of the isomers, the C–COOH bond is apparently broken selectively. There is, however, no clear correspondence of yields among the products of the decomposition. The position of substitution influences the relative yield of products, although differences between isomers do not appear to be simply a function of the proximity of the groups.

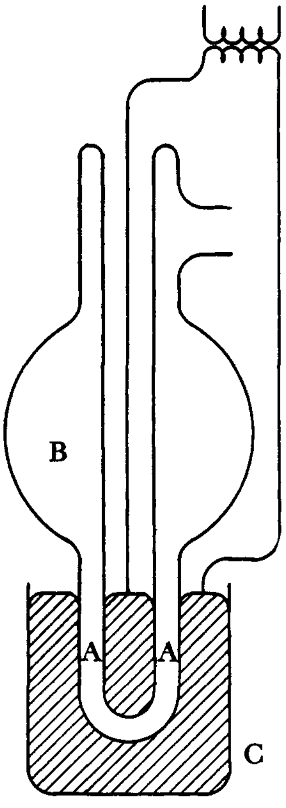

Fig. 1.—Discharge chamber.

Experimental

The toluic acids were obtained from Eastman Kodak Company and were recrystallized from alcohol and sub-

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(1) Department of Chemistry, University of California.

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(3) M. Burton, *J. Phys. Chem.*, **51**, 786 (1947).

(4) C. W. Sheppard and V. L. Burton, THIS JOURNAL, **68**, 1636 (1946).

(5) I. A. Breger, *J. Phys. and Colloid Chem.*, **52**, 551 (1948).

(6) R. E. Honig, *Science*, **104**, 27 (1946).

(7) G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, New York, N. Y., 1949.

limed *in vacuo;* melting points were: ortho 102.5–103°, meta 110.5–111°, para 177–178°.

The discharge chamber is shown in Fig. 1. It was connected through stopcocks to a manifold and to a product gas storage bulb. During a run, the acids were distilled through the discharge which occurred in the region A. The surface B acted as an air condenser for the distillate. The acids were kept at the melting point by the mercury bath C which also served as one of the electrodes. The discharge was produced by a Tesla-type transformer which gave a peak potential of 7000 volts at a frequency of 0.5 megacycle. A Toepler pump was used to transfer the product gases from the storage bulb to a micro gas analyzer.[8] The entire system could be evacuated to 10^{-5} mm. by a mercury diffusion pump which was connected to the system through a trap immersed in liquid air.

In a typical run approximately 3 g. of purified acid was placed in the discharge chamber which was then sealed into the vacuum system. The acid was degassed by alternate freezing and thawing under vacuum. After adjusting the temperature of the mercury bath to the melting point of the acid, the discharge was started and continued until the pressure in the product bulb reached 3 mm. This pressure was equivalent to 70 ml. of gas at standard conditions.

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(8) C. N. Stover, W. S. Partridge and W. M. Garrison, *Anal. Chem.*, **21**, 1013 (1949).

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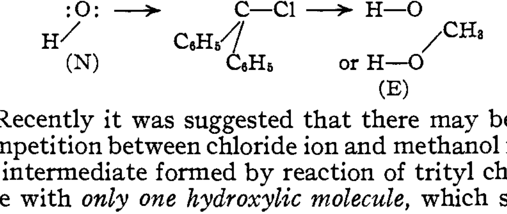
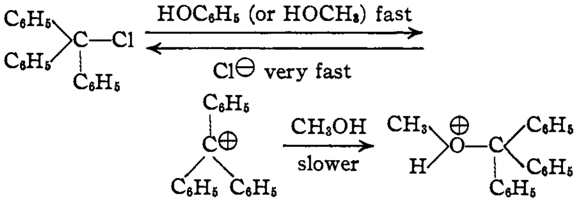
Concerted Displacement Reactions. IV. Halide Exchange of Triphenylmethyl Halides in Benzene Solution[1]

BY C. GARDNER SWAIN

The first paper of this series showed that the methanolysis of triphenylmethyl (trityl) chloride in benzene solution was third order, practically unaffected by the concentration of tertiary amines or tertiary ammonium chlorides, but accelerated seven-fold by the presence of 0.05 *M* phenol, a substance which reacted with trityl chloride only very slowly by itself. The *rate-determining step* appeared to be a concerted, push-pull process, requiring two hydroxylic molecules, one acting as a nucleophilic reagent (N) to attack carbon and the other acting as an electrophilic reagent (E) to attack halogen.[2]



Recently it was suggested that there may be a competition between chloride ion and methanol for an intermediate formed by reaction of trityl chloride with *only one hydroxylic molecule,* which solvates only the halide ion.[3]



This scheme would also explain the third-order kinetics. It was suggested that if this mechanism holds, increasing the concentration of tertiary ammonium chlorides in the solution should increase the rate of the very fast reverse reaction. The fact that no such "mass effect," or decrease in the net forward rate was observed experimentally required that there be a fortuitous compensation by an equally large "salt effect" by these tertiary ammonium chlorides on the fast, forward ionization step.

The existence of such a competition has now been disproved experimentally by replacing the tertiary ammonium chlorides by tertiary ammonium sulfonates, which cannot give a "mass effect," but should still show the large "salt effect," if one exists with tertiary ammonium salts of this type. The effect on the rate was found to be negligibly small.

Quinolinium benzenesulfonate, *p*-toluenesulfonate, naphthalene-β-sulfonate and quinolinium *dl*-camphorsulfonate are all very sparingly soluble in benzene (*ca.* 0.01 *M*). However, quinolinium *d*-camphorsulfonate, proved to be thirty times as soluble as the *dl* form. This salt could be highly purified, had a decomposition point of 118–120° and was extremely soluble in water. *Anal.* Calcd. for $C_{19}H_{23}NSO_4$: C, 63.13; H, 6.41. Found: C, 63.29; H, 6.46. With 0.105 *M* trityl chloride, 0.108 *M* quinoline and 0.107 *M* methanol, the initial rate of methanolysis was increased *less than 25%* by either 0.031 *M* or 0.093 *M* concentrations of the anhydrous salt.[4]

Thus there is no competition between tertiary ammonium chlorides and methanol for any intermediate in the methanolysis in benzene solution.[5]

The foregoing experiments, although sufficient to rule out the existence of such a competition, are not a real test of salt effects in benzene because (1) tertiary ammonium salts are hydrogen bonded

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[1] This work was supported by the Office of Naval Research.

[2] Swain, THIS JOURNAL, **70**, 1119 (1948). The kinetics shed light on only the rate determining step, which does not necessarily give the final product directly. It is possible that some methanol molecule other than N may bond covalently with carbon in a subsequent fast step.

[3] This was proposed at the American Chemical Society convention at Atlantic City, September 21, 1949, by Dr. Jack Hine; *cf.* "Abstracts of Papers," p. 83M.

[4] The solubilities of quinolinium chloride were 0.01, 0.015 and 0.033 *M* in the presence of 0.00, 0.031 and 0.093 *M* quinolinium *d*-camphorsulfonate, respectively. The rates fell off less rapidly than usual toward the end in the runs with added sulfonate, suggesting that a quinolinium salt (or the acid in equilibrium with it) may serve as the electrophilic reagent E instead of methanol to a small extent. It should be emphasized that the concentration of tertiary ammonium salts in these experiments was purposely increased to a considerably higher level (0.126 *M*) than was present in any previous work. In the previous work, total salt concentrations as low as 0.0015 *M* were used.

[5] It has occurred to us that a more difficultly discernible kind of reversal may be occurring by a first order *intramolecular* reaction between the carbonium ion and solvated chloride ion of a *single* ion pair. However, until intermediates are demonstrated by successful capture by external reagents other than methanol or by spectral methods, we prefer the simpler original picture of concerted back and front side attack.