of hydrochloric acid, hydrobromic acid and perchloric acid were employed. With all of these eluting agents the separation of tracer amounts of americium and curium is essentially the same as with citrate. Figure 2 shows an elution with 6 *M* hydrochloric acid run with the same column as that used for the citrate run whose results are shown in Fig. 1. It is apparent that there has been a shift in the relative rate of elution of the two actinide elements with respect to the rare earths. Elution with solutions of still higher hydrochloric acid concentration shows the very marked effect of hydrochloric acid concentration on the time of elution of americium and curium with respect to the rare earths. This is illustrated in Figs. 3 and 4 which show elutions with 9 and 13.3 *M* hydrochloric acid, respectively. It will be noted that with 9 *M* hydrochloric acid americium and curium are eluted with the heavy rare earths while with 13.3 *M* hydrochloric acid they have moved out well ahead of all the rare earths.

Examination of Figs. 2, 3 and 4 will also reveal another striking fact. It will be noted that with 6 *M* hydrochloric acid americium and curium are eluted in their normal order, that is, curium is eluted before americium in the order that would be predicted from the size of their ions and the order of elution of the rare earths. In 9 *M* hydrochloric acid the americium and curium are eluted together while in 13.3 *M* hydrochloric acid the order of elution is reversed, the americium coming off slightly ahead of the curium while the rare earths maintain their normal order throughout the whole range of hydrochloric acid concentrations.

Discussion of Results

The effects found were of a much greater magnitude than anything anticipated when the experiments were undertaken. Thus a single elution with 13.3 *M* hydrochloric acid separates americium and curium from all the rare earth elements. The relatively large differences in the rate of elution of americium and curium and the first rare earth element makes rapid elution possible. By using columns 5 cm. long and flow rates of 2 ml./sq. cm./min. a separated americium–curium fraction can be obtained in about twenty minutes. Although the separation of curium from americium is not good, some fractionation does occur and this is very useful in attempting to identify short-lived isotopes of these elements.

In addition to the very useful nature of this result as an analytical tool, the anomalous behavior of americium and curium suggests some very interesting speculation in regard to its explanation.

On elution with solutions of hydrochloric acid of increasing concentration, americium and curium behave as though at high hydrochloric acid concentration there are on the average several more chloride ions in the complex ions involving americium and curium than in those of the rare earth elements. In view of the similarity in size and charge of the americium and curium and the rare earth ions, this suggests that in addition to the interactions which the rare earths show with chloride ion perhaps americium and curium form weak covalent coördination complexes involving large numbers (say 6) of chloride ions.

One of the most obvious differences between the actinide and the lanthanide elements is the relative stability of the f orbitals. Thus in the actinide transition series the 5f have probably just become stable with respect to the 6d orbitals at uranium and are only a little more stable at americium and curium. On the other hand, in the rare earth elements the 4f are already quite stable with respect to the 5d orbitals at cerium. This suggests that perhaps the 5f orbitals of some of the actinides can contribute to hybridized covalent bond orbitals, while in the rare earths the very stable and more deeply buried 4f orbitals are not available. Thus if the covalent complex ion of americium were slightly more stable than that of curium, elution with increasing concentrations of hydrochloric acid would result in both americium and curium moving up with respect to the rare earths, but americium moving slightly faster, as is observed to be the case.

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The Reaction of Tributylacetyl Chloride and Anhydrous Cuprous Cyanide

BY NATHAN SPERBER AND ROSEMARIE FRICANO

As part of a related problem, tributylacetyl cyanide was required as an intermediate. Acyl cyanides have been prepared by the reaction of an acid chloride with anhydrous cuprous cyanide[1] or silver cyanide.[2] When tributylacetyl chloride was treated with dry cuprous cyanide, a product was obtained which contained no nitrogen[3] or chlorine, decolorized bromine water and had a lower boiling point and viscosity than did tributylacetyl chloride. On the basis of the qualitative tests and quantitative analysis, it appeared that rupture of the acyl chloride group occurred at the quaternary carbon with the formation of an olefin. The latter was identified as 5-butylnonene-4 by comparison with an authentic sample prepared[4] by the dehydration of tributylcarbinol. On catalytic reduction, the olefin absorbed one mole of hydrogen to yield 5-butylnonane.[5] In contrast, when trimethylacetyl chloride was refluxed with cuprous cyanide, trimethylacetyl cyanide was isolated.[6]

Experimental

Tributylacetyl Chloride was prepared by the reaction of tributylacetic acid[7] and thionyl chloride; yield 90%, b. p.

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[1] Tschelinzeff and Schmidt, *Ber.*, **62**, 2210 (1929).

[2] Hüber, *Ann.*, **120**, 330 (1861); Moritz, *J. Chem. Soc.*, **39**, 13 (1881).

[3] In one experiment, the tributylacetyl cyanide was apparently obtained. *Anal.* Calcd. for $C_{15}H_{27}ON$: N, 5.91. Found: N, 6.01. This product could not be obtained in subsequent experiments.

[4] Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933); Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

[5] Ivanov, *Bull. soc. chim.*, [4] **37**, 287 (1925).

[6] Trimethylacetyl chloride decomposes in the presence of aluminum chloride to yield carbon dioxide, hydrogen chloride and the olefin polymer (Böeseken, *Rec. trav. chim.*, **29**, 94 (1910). The same reaction occurs when an acyl chloride is passed over heated nickel (Mailhe, *Compt. rend.*, **180**, 111 (1925)).

[7] Whitmore, *et al.*, THIS JOURNAL, **63**, 643 (1941); Sperber, Papa and Schwenk, *ibid.*, **70**, 3091 (1948).

120-121° (5 mm.), n_{D}^{22} 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_{D}^{26} 1.4369 (lit.[4] b. p. 60° (1.2 mm.), n_{D}^{20} 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_{D}^{27} 1.4245, colorless oil (lit.[5] b. p. 217.5-218.5°, n_{D}^{19} 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_{D}^{27} 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_{D}^{25} 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

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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.

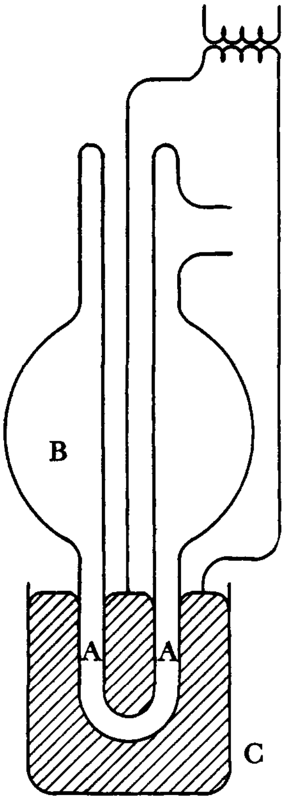

Fig. 1.—Discharge chamber.

Experimental

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

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[2] Radiation Laboratory, University of California.

[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.