The Reaction of Succinic and Glutaric Acid with Amines

BY G. BROOKE HOEY[1] AND CHAS. T. LESTER

A comparative study of imide formation has been made using glutaric acid and succinic acid and a variety of primary amines. The object was not to realize the maximum yield for any given imide, but to note the differences between the two acids when allowed to react under the same conditions. Three sets of conditions were used: (A) sealed tube reactions, (B) heating amine and acid and allowing the water formed to distil, (C) azeotropic removal of water, using *p*-cymene. The results are summarized in Table I. Table II contains analytical data on the new compounds prepared.

From a practical synthetic viewpoint it is evident that succinimides are more readily prepared than glutarimides by any of these methods. Method C proved unexpectedly satisfactory for the preparation of solid imides. While the yields are not high, the procedure is easily set in operation, demands little attention and gives products less discolored, and hence more easily purified, than method A or B.

TABLE I

R	Method	imide Yield %^{a}		Yield^{a,b} glutaric diamide, %	M.p., °C. imide		
		Succin-	Glutar-		Succin-	Glutar-	Diamide
Isopropyl	A	20	20	0^{c}	61^{d}	^{e}	..
Isopropyl	B	...	26	0^{c}	..	^{e}	..
n-Butyl	A	20	0^{f}	63	^{g}	...	151
n-Butyl	B	43	25	0	^{g}	^{h}	..
n-Amyl	A	...	0	90	..	...	137
n-Heptyl	A	...	0^{f}	73	..	...	144
Phenyl	A	20	0	20	155^{i}	...	225^{j}
Phenyl	B	20	0	20	155^{i}	...	225^{j}
Phenyl	C	24	...	...	155^{i}	...	..
o-Tolyl	A	...	0	20	..	...	223^{j}
o-Tolyl	C	21	11	0	101^{k}	132	..
m-Tolyl	A	...	0	12	..	...	135
p-Tolyl	A	21	0	20^{l}	150^{k}	...	215^{j}
p-Tolyl	A	...	6^{m}	0	..	176	..
2-Biphenyl	A	15	0	20	132	...	163^{n}
2-Biphenyl	C	22	0^{o}	0^{o}	132^{p}	...	..
4-Biphenyl	A	21	0	0	247	...	..
4-Biphenyl	B	21	0	0	247^{p}	...	..
2-Pyridyl	C	34^{q}	^{q,r}	^{q,r}	137	...	..
2-(3-Me-pyridyl)	C	31^{q}	^{q,r}	^{q,r}	118^{s}	...	..
2-(4-Me-pyridyl)	C	65^{q}	^{q,r}	^{q,r}	117^{s}	...	..
2-(5-Me-pyridyl)	C	64^{q}	^{q,r}	^{q,r}	168	...	..
2-(6-Me-pyridyl)	C	45^{q}	29	0	143	192	..

[a] Yields are based on pure product. Zero yield means no evidence of the compound was found during the purification procedure. [b] No diamide of succinic was found in any of its reactions. [c] The tarry residue from distillation of the imide was not examined for diamide. [d] J. Tafel and M. Stern, *Ber.*, **33**, 2233 (1900). [e] B.p. 121–124°, at 14 mm. [f] A total of 2–3 ml. of product was accumulated from 7 runs. If this were pure imide, it would represent a 0.5–1% yield. [g] B.p., 137–139° at 12 mm. [h] B.p. 136–138°, at 10 mm. [i] A. Laurent and C. Gerhardt, *Ann.*, **68**, 27 (1948). [j] C. R. Barnicoat, *J. Chem. Soc.*, 2926 (1927). [k] A. J. Taylor, *Ber.*, **8**, 1225 (1875). [l] Average of 7 runs at 230–250° for 8 hrs. [m] A single run at 270–290° for 10 hr. [n] E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 134 (1945) (*C. A.*, **40**, 878 (1946)). [o] The glutaric acid was quantitatively recovered. [p] Identity established by mixed m.p. with product of method A. [q] Method A gave inseparable mixture of compounds. [r] Method C gave a product whose m.p. indicated purity; the nitrogen analysis was unsatisfactory. [s] Mixed m.p. of 3- and 4-methylpyridyl imide, 80–95°.

TABLE II

ANALYSIS OF NEW^{a} IMIDES AND DIAMIDES

R	N,^{b} % Calcd.	N,^{b} % Found
Succinimides		
n-Butyl	9.03	8.70, 8.71^{c}
2-Biphenyl	5.58	5.31
4-Biphenyl	5.58	5.33
2-Pyridyl	15.91	15.76
2-(3-Me-pyridyl)	14.73	14.64
2-(4-Me-pyridyl)	14.73	14.87
2-(5-Me-pyridyl)	14.73	14.45
2-(6-Me-pyridyl)	14.73	14.87
Glutarimides		
Isopropyl	9.03	8.78, 8.80^{c}
n-Butyl	8.23	8.15
o-Tolyl	6.89	7.06
p-Tolyl	6.89	6.77
2-(6-Me-pyridyl)	13.72	13.46
Diamides		
n-Butyl	11.56	11.57
n-Amyl	10.36	10.23
n-Heptyl	8.58	8.81
m-Tolyl	9.03	9.24

[a] All liquid products were analyzed as a check on purity, even though previously reported. [b] Determined by Dumas method. [c] Separate analyses on product from two different methods.

Experimental[2]

Method A.[3]—The amine and acid (0.03 mole of each) were sealed in a Carius tube and heated in a sand-bath at 230–260° for 8 to 10 hr. In cases where the two acids were reacted with a common amine the tubes were placed side by side. After cooling and opening the tube, the contents were processed in one of two ways. (1) If solid, the contents were washed out with alcohol and crystallized to constant m.p. from water or an alcohol–water mixture. This frequently necessitated four or five crystallizations, including decolorizing with charcoal. (2) If liquid, the contents were dissolved in ether and three corresponding runs combined. After drying the ether solution over anhydrous magnesium sulfate, the ether was removed by distillation and the residue distilled under reduced pressure. In all the reactions involving aliphatic amines the contents of the tubes, liquid or solid, were extracted with ether, in which the imides, but not the diamides, are readily soluble. The ether extracts and residual solids, were then separately processed as in (1) and (2) above.

Method B.—A mixture of 0.01 mole each of acid and amine was placed in a 50-ml. distilling flask or a 20-cm. test-tube and heated slowly to a temperature of 125–175°. The temperature was maintained at this level for 3–5 hr., or until no further distillation was evident. After cooling, the residue was purified, if a solid, by method A(1). If liquid, the residue was distilled under reduced pressure, three runs combined and purified as in Method A(2).

Method C.[3]—A solution of 0.1 mole each of acid and amine in 1000 ml. of *p*-cymene was placed in a 2000-ml. flask equipped with a reflux condenser and water separator. The *p*-cymene was kept at a temperature that permitted steady refluxing until there was no further sign of water distillation. This usually required 5 to 6 hr. The product was isolated by repeatedly cooling and concentrating the *p*-cymene

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[1] Taken from the M.A. Thesis of G. B. Hoey, Emory University, 1950.

[2] All b.p.'s. and m.p.'s. reported in this work are uncorrected.

[3] Unless otherwise indicated these preparations were run in triplicate.

solution.[4] The solid which precipitated was removed by filtration and purified by crystallization from alcohol and water or benzene and petroleum ether.

Acknowledgment.—We wish to thank Dr. E. E. Reid for his interest and helpful suggestions in connection with this work.

[4] In general 700 ml. of *p*-cymene was distilled and the residue was cooled to 0°.

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RECEIVED MARCH 5, 1951

Anion Exchange of Zirconium, Hafnium, Niobium and Tantalum in Hydrochloric Acid Solutions

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The behavior of fluoride-containing complex ions of zirconium, hafnium, niobium and tantalum when eluted from anion exchange resins with mixtures of hydrochloric and hydrofluoric acids has been described and the nature of these ions has been discussed on several occasions.[1,2] It has been found in this Laboratory by the present writers and by D. A. Orth (for zirconium) that zirconium, hafnium, niobium and tantalum form complex chloro-ions in strong hydrochloric acid which can be exchanged on anion exchange resins. Some of the characteristics of these exchanges have been studied and are reported here.

Experimental

Radioactive tracers, with the exception of Zr^{89}, were obtained from the Isotopes Branch, U. S. Atomic Energy Commission. Zirconium tracer solutions were prepared from both Zr^{95} and from Zr^{89} produced by 100 mev. proton bombardment of niobium foil in the 184-inch cyclotron. The Zr^{95} tracer was separated from the daughter Nb^{95} by carrying the latter on precipitated manganese dioxide in a manner similar to that already reported.[3] This tracer in nitric acid was then combined with a weighed amount of zirconium dioxide and the whole converted to a solution in concentrated hydrochloric acid without other anions. The zirconium tracer for the batch equilibrations was prepared from Zr^{89} (80 hr. half-life) in order to avoid interference from Nb^{95} which would grow in if Zr^{95} were used. It was chemically separated by the method of Hyde and O'Kelley,[4] and stored in concentrated hydrochloric acid. Hafnium tracer solutions in concentrated hydrochloric acid were prepared from hafnium dioxide containing Hf^{181} and were about 0.003 molar in carrier hafnium. The Nb^{95} tracer solutions were prepared from the material carried on the manganese dioxide in the Zr^{95} purification. The small amount of Zr^{95} activity which accompanied the Nb^{95} was removed by extraction with thenoyltrifluoroacetone,[3] and the purified Nb^{95} was finally made up in concentrated hydrochloric acid. An easier method for separating Zr^{95} and Nb^{95} was found during the course of this investigation and is reported below. This method was used for the separation in the later stages of the study.

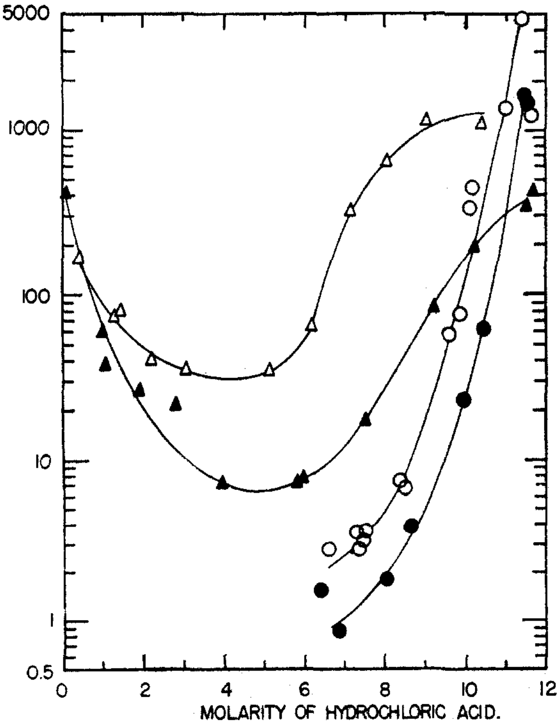

Fig. 1.—Dependence of the distribution coefficient at 25° on the hydrochloric acid concentration: △, niobium; ▲, tantalum; ○, zirconium; ●, hafnium.

The Ta^{182} tracer was received in solution as potassium tantalate and contained carrier tantalum. About 0.2 ml. of this solution was heated with 1 ml. of concentrated hydrochloric acid containing a few drops of concentrated hydrofluoric acid. Evaporation to small volume, with added hydrochloric acid, was repeated several times to drive off hydrofluoric acid. The solution was then made up in 9 *M* hydrochloric acid and the activity was adsorbed on a column of Dowex-2 anion exchange resin to get rid of potassium. The Ta^{182} activity was then washed from the column with 2 *M* hydrochloric acid. The activity of this solution compared to the specific activity of the original solution indicated the concentration of carrier tantalum to be about 1.2 micrograms per ml., or 7×10^{-6} molar.

The values of K_D at different hydrochloric acid concentrations were obtained by equilibrating 2.1–2.3 ml. of tracer solution with 15–300 mg. of 60–100 mesh Dowex-2 resin, oven-dried at 70°, in a plastic vial. The acid concentration of the solution was determined by titration after equilibration. The time required to reach equilibrium is discussed below. All equilibrations were made in a constant temperature bath at 25°.

The anion exchange separation of zirconium and hafnium was carried out by elution from the same resin with 9.0 *M* hydrochloric acid, using a lucite column 11 cm. in length and 6.5 mm. i.d., at a rate of 10–12 ml. per hour. A mixture of 3.8 mg. each of zirconium and hafnium, with tracers, in 1.2 ml. of concentrated hydrochloric acid was first adsorbed slowly at the top of the column for this purpose. Identification of the two peaks in the resulting elution curve

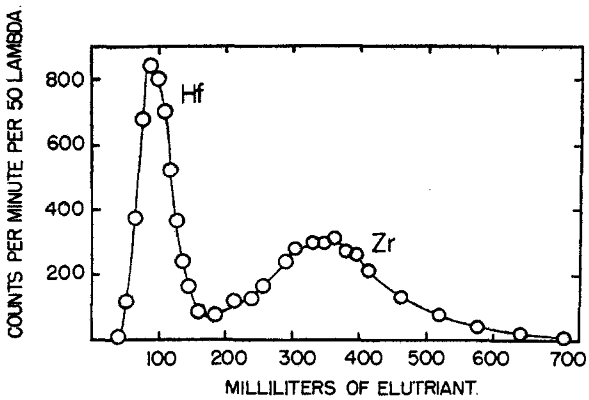

Fig. 2.—Elution of chlorozirconate and chlorohafniate with 9.0 *M* hydrochloric acid.

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[1] K. A. Kraus and G. E. Moore, THIS JOURNAL, **71**, 3263, 3855 (1949); **73**, 9, 13 (1951).

[2] E. H. Huffman and R. C. Lilly, *ibid.*, **71**, 4147 (1949); **73**, 2902 (1951).

[3] R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

[4] E. K. Hyde and G. D. O'Kelley, University of California Radiation Laboratory Report UCRL-1064 (December, 1950); accepted for publication in *Chem. Rev.*