and have found the rate to be measurable. In view of current interest in electron transfer reactions, it is felt that a preliminary report may be of interest at this time.

Oak Ridge cerium 144 (275 day half-life) was purified by the procedure described by Newton.[2]

Several experiments were performed in which a diffusion separation[3] was employed. The ceric and cerous concentrations were each 0.005 *f*, the solvent was variously 1 *f* sulfuric acid, 2 *f* perchloric acid, or 6 *f* perchloric acid. The results indicated complete exchange within two hours,[4] but the poor separation factor and the possibility of reduction of ceric ion in the diffusate indicated that another approach would be desirable.

The second method employed was to extract ceric cerium from nitric acid solution with diethyl ether. Stock solutions of active cerous and inactive ceric nitrates were mixed in a thermostated bath, and the ceric nitrate was extracted into analytical reagent ether. The ethereal phase was washed with nitric acid, and the cerium reextracted into water. The resultant solution was diluted to constant volume and counted with a dipping Geiger–Müller tube. In all cases the 17-minute praseodymium daughter was allowed to grow into the sample before counting. It was found that no significant amount of cerous ion is extracted and that the extraction of ceric nitrate is essentially complete.

The results obtained with solutions 6.18 *f* in nitric acid are given in Table I. Ceric concentration was determined by titration with ferrous ion; cerous by a second titration after oxidation with ammonium peroxysulfate and silver catalyst.

The expected exponential time dependence[5] of the extent of exchange was observed in each run.

TABLE I

Run	Cerous conc., *f*	Ceric conc., *f*	Temp., °C.	Half time of reaction, minutes	*k*, mol.$^{-1}$ min.$^{-1}$
1	0.00198	0.00187	25.03 ± 0.02	11.2 ± 0.3	16
2	.00198	.00187	0.0 ± 0.2	88 ± 4	2.0
3	.00198	.0187	.0 ± 0.2	20.0 ± 0.5	1.7
4	.0198	.00187	.0 ± 0.2	16.7 ± 0.5	1.9

From these data we calculate the experimental energy of activation to be 13.4 ± 0.7 kcal. and conclude that the reaction is first order with respect to both cerous and ceric concentrations. The last column gives the calculated bimolecular rate constant.

Experiments are in progress to determine the effect of concentration of reactants, ionic strength, and nitrate and hydrogen ion concentration. Additional experiments are planned with sulfuric and perchloric acid systems.

We are indebted to Dr. Jerome J. Howland, Jr., for information about the ether extraction of cerium.

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RECEIVED APRIL 11, 1949

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[2] A. S. Newton, *Phys. Rev.*, **75**, 17 (1949).

[3] C. L. Van Alten and C. N. Rice, THIS JOURNAL, **70**, 883 (1948).

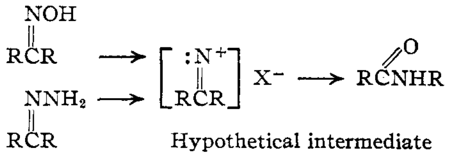
[4] Through the kindness of Professor A. C. Wahl, we have learned that similar conclusions have been reached in his laboratory.

[5] (a) H. A. C. McKay, *Nature*, **142**, 997 (1938); (b) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

THE REARRANGEMENT OF HYDRAZONES

Sir:

Structural and chemical analogy suggests that ketone hydrazones should undergo a rearrangement similar to the Beckmann rearrangement of ketoximes. Consideration of the mechanism of the Beckmann rearrangement[1] suggests a common intermediate or reaction path



Sidgwick,[2] however, states that there is no general reaction of the hydrazones, such as the Beckmann transformation of oximes. Search of the literature also has not revealed any examples.

Attempted deamination with nitrous acid, which is similar to the semi-pinacolinic, deamination process of McKenzie[3] yielded only the ketone; attempted deamination with sodium nitrite in glacial acetic acid, without mineral acid, yielded chiefly the azine.

It was observed by electrometric titration that benzophenone hydrazone is an extremely weak base which fails to titrate sharply in aqueous solution with mineral acids. Instead, it undergoes moderately rapid and quantitative hydrolysis to the ketone. Accordingly, it appeared that the hydrazone had failed to undergo "diazotization." It was thus indicated that a relatively strong, anhydrous acid should be used as a medium for "diazotization," not only to prevent hydrolysis but also to convert the hydrazone to a salt which would be "diazotizable."[4]

An equivalent of benzophenone hydrazone was dissolved in twenty times its weight of concentrated sulfuric acid, and the mixture cooled to 0°. A slight excess of one equivalent of solid sodium nitrite was added to the stirred mixture in small enough portions to keep the temperature below 8°. After the completion of the addition (sixty minutes), the mixture was poured on to ice, neutralized with ammonium hydroxide, and the pre-

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[1] Pearson and Ball, *J. Org. Chem.*, **14**, 118 (1949).

[2] Taylor and Baker in Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1937, p. 397.

[3] McKenzie and Mills, *Ber.*, **62B**, 284 (1929).

[4] Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1948, p. 315.

cipitate purified in the usual manner. There was obtained an essentially quantitative yield of benzanilide, m. p. 160.5–162.0°. This was identified and distinguished from the azine and other possible products by mixture melting point experiments and hydrolysis to benzoic acid and aniline.

Extensions of an obvious nature are being carried out on the rearrangement of other hydrazones and of other hydrazine derivatives under these conditions.

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RECEIVED MARCH 31, 1949

THE DIELECTRIC CONSTANT OF WATER AT VERY HIGH TEMPERATURES

Sir:

A property of liquid water that is very important in modern solution theories is its dielectric constant. Since no data are available for temperatures above 100° we have made a number of measurements of the value of this constant at temperatures up to 375°. An all-platinum cell enclosed in a stainless steel bomb was used with a high frequency resonance measuring circuit for the range 70–250 megacycles. The temperature was determined with thermocouples calibrated against a platinum resistance thermometer. In Fig. 1 the dotted line represents values of the dielectric constant predicted from the equation of Akerlof (THIS JOURNAL, **54**, 4125 (1932))

$$\log D = 1.9461 - 0.00205t$$

The full drawn curve represents our experimental values at temperatures up to 325°. The two curves practically coincide up to temperatures of about 250°.

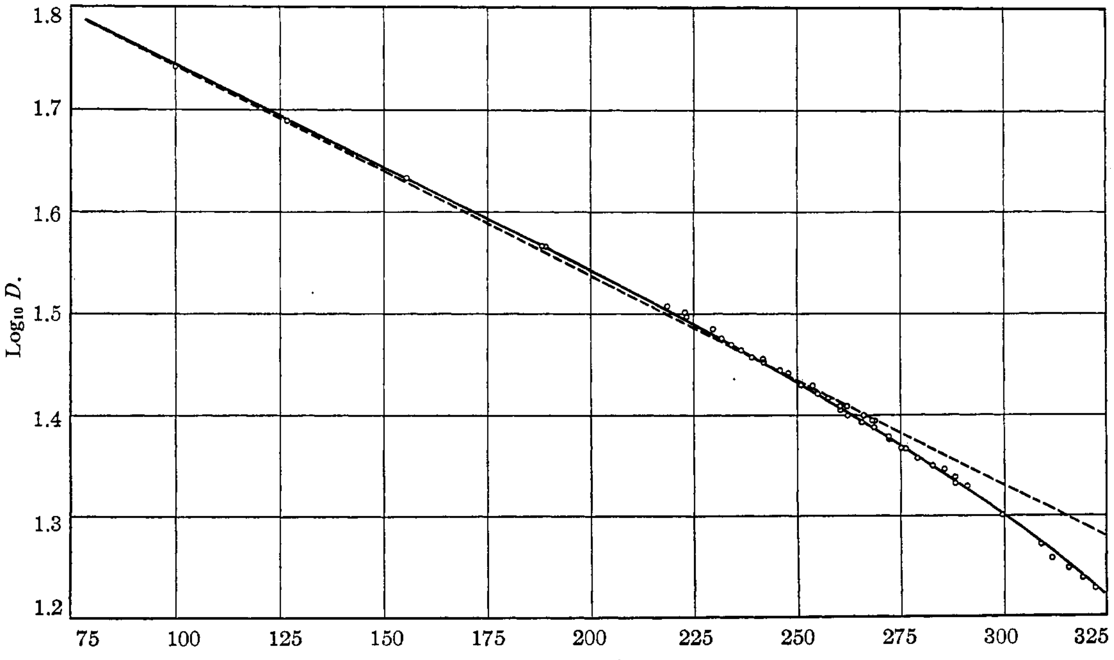

Fig. 1.

We wish to express also in this place our sincere appreciation for the aid given us by Mr. Fred Denig, Vice President of the Koppers Company.

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G. C. AKERLOF

RECEIVED MARCH 7, 1949

REARRANGEMENT OF CARBON ATOMS IN ALKYL DERIVATIVES

Sir:

Carbon-14 has been used as a tracer to detect rearrangements of carbon atoms in *t*-butyl and *t*-amyl derivatives.

$$\underset{\text{I}}{(CH_3)_3C^{14}X} \rightleftarrows \underset{\text{II}}{(CH_3)_2(C^{14}H_3)CX}$$

$$\underset{\text{III}}{(CH_3)_2C^{14}XCH_2CH_3} \rightleftarrows \underset{\text{IV}}{(CH_3)_2CXC^{14}H_2CH_3} \rightleftarrows$$

$$\underset{\text{V}}{(CH_3)_2CXCH_2C^{14}H_3} \rightleftarrows \underset{\text{VI}}{C^{14}H_3(CH_3)CXCH_2CH_3}$$

Rearrangement of 2-methyl-2-chlorobutane-2-C^{14} (III, X = Cl) proceeded under the influence of aluminum chloride. Using conditions where 59% of the chloride was recovered the composition of the product was 64% of III (X = Cl), 35% of IV (X = Cl) and about 1% of V (X = Cl). Less than 0.1% of VI (X = Cl) was detected.