The Electrical Conductivity of Uranyl Fluoride in Aqueous Solution

By Robert D. Brown, W. B. Bunger, William L. Marshall and C. H. Secoy

Received October 7, 1953

The conductivity of uranyl fluoride in aqueous solution has been measured in various concentrations at 0°, 25°, 50° and 90°. The only previous work of this nature encountered in the literature is that of Dean[1] who measured the conductivity of uranyl fluoride solutions at 25° in concentrations of 0.125 N and above. The present work is in excellent agreement with his report.

Experimental

The conductivity apparatus used for these measurements has been described previously.[2] Measurements of *p*H were made at 25° with a Beckman model N *p*H meter.

To prepare the solutions for conductance experiments, anhydrous uranyl fluoride, of the same purity as used by Johnson and Kraus,[3] was dissolved in water to give a 1 N solution, from which less concentrated solutions were prepared by dilution. More concentrated solutions were prepared by individual weighing and dissolving.

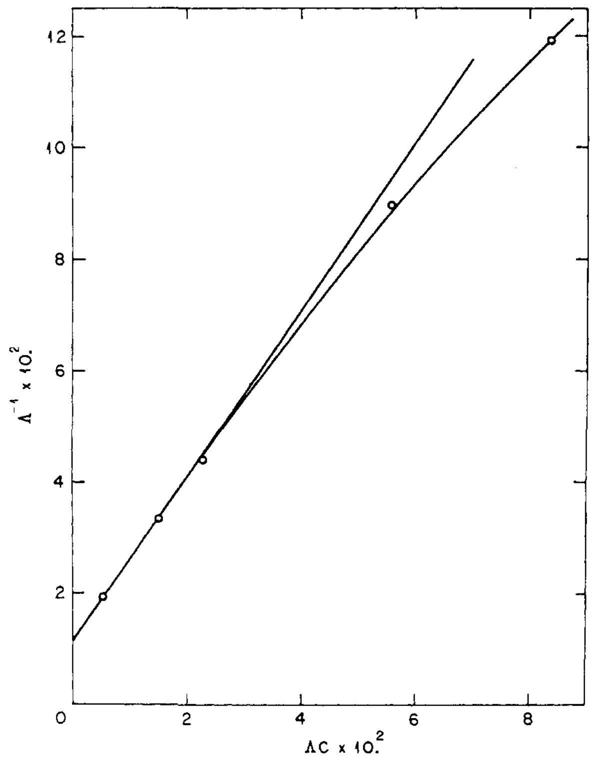

Fig. 1.—Kraus and Bray extrapolation plot for uranyl fluoride; at 25°, —$\Lambda°$ = 82.

Results and Discussion

The conductances of uranyl fluoride in aqueous solution at the specified temperatures and concentrations are shown in Table I. It is evident from the conductance values and from the shape of the plots of Λ *vs.* $C^{1/2}$, that UO_2F_2 in aqueous solution is a very weak electrolyte. It is much less conductive than an equivalent solution of uranyl sulfate. The percentage increase in conductance over the range 0 to 90° is much greater for UO_2F_2 than for UO_2SO_4. This increase, however, is approximately what one would expect from the decrease in the viscosity of the solvent, Fig. 2. On the basis of this consideration it would appear that there has been little or no increase in ionization in going from 0 to 90°.

Table I

Conductivity Data

Concentration[a] (equiv./liter)	Λ, ohm^{-1} cm.^{2} equiv.$^{-1}$ 0°	25°	50°	90°
0.0001	34.44	73.54	...	...
.0005	18.37	35.70	62.48	104.2
.001	12.46	26.10	44.22	71.3
.005	6.16	12.31	19.51	30.4
.01	4.61	9.17	14.41	22.7
.05	2.73	5.43	8.60	13.52
.1	2.37	4.74	7.50	11.88
.5	1.87	3.75	5.96	9.50
1.0	1.60	3.22	5.10	8.15
3.0			3.12	4.91
6.0			1.40	2.27

[a] All concentrations are on 25° basis.

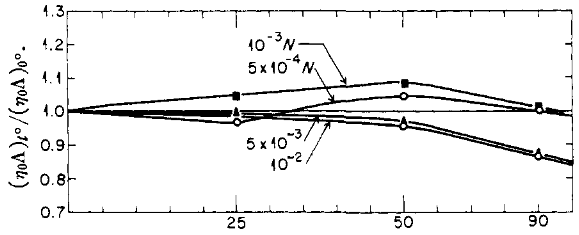

Fig. 2.—$\eta_0\Lambda$ of uranyl fluoride as a function of t,°C.

The data at 25° have been corrected for the conductance of hydrogen ion present as a result of hydrolysis,[4] but corrections for other possible ionic species have not been attempted. The corrected data are shown in Table II. Extrapolation of these data by the procedure of Kraus and Bray[5] (shown in Fig. 1) leads to a value of 87 for $\Lambda°$ and, using a value of 55 for $\lambda^\circ_{F^-}$,[6] gives $\lambda^\circ_{UO_2^{++}}$ = 32.

Table II

Corrected Conductance Data, 25°

C[a]	*p*H	Λ'[b]	α	$y_\pm^2$	$K \times 10^5$
0.0001	5.22	52.4	0.6120	0.9566	4.63
.0005	5.09	30.02	.3486	.9284	4.34
.001	5.02	22.76	.2675	.9125	4.40
.005	4.79	11.17	.1340	.8670	4.54
.01	4.65	8.39	.1019	.8398	4.85
.05	4.20	4.99	.0638	.7429	8.07
.1	3.94	4.34	.0636	.6666	13.5
.5	3.25	3.36			
1.0	2.92	2.80			

[a] C, equivalents per liter. [b] Λ', equivalent conductance.

---

(1) G. R. Dean, "Properties of Uranyl Fluoride," Metallurgical Project Report No. CC2092 (September, 1944).

(2) R. D. Brown, W. B. Bunger, W. L. Marshall and C. H. Secoy, This Journal, **76**, 1532 (1954).

(3) J. S. Johnson and K. A. Kraus, *ibid.*, **74**, 4436 (1952).

(4) B. B. Owen and R. W. Gurry, *ibid.*, **60**, 3074 (1938).

(5) C. A. Kraus and W. C. Bray, *ibid.*, **35**, 1315 (1913).

(6) T. Shedlovsky, *ibid.*, **54**, 1410 (1932). $\lambda^\circ_{F^-}$ = 55 at 25° was estimated from $\Lambda°_{KF}$ = 111.2 at 18° and $\Lambda°_{K^+}$ = 73.52 at 25° using the equation $\lambda°_t = \lambda°_{25°}[1 + \alpha(t - 25)]$ and assuming $\alpha = 1.9 \times 10^{-2}$.

A value of $\lambda^{\circ}_{\mathrm{UO_2^{++}}} = 39$ was obtained from uranyl sulfate data[2] corrected only for the conductance of hydrogen ions.

Values for the dissociation constant, K, given in Table II were calculated from the corrected conductance data using theoretical activity coefficients and assuming that the dissociation reaction was represented by

$$UO_2F_2 \rightleftharpoons UO_2F^+ + F^-$$

Although the constancy of the K values at the lower concentrations is believed to be of significance, the dissociation of uranyl fluoride is most probably more complex than was assumed. The agreement may be largely fortuitous.

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

The Heterogeneous Carbon Monoxide-Ozone Reaction on Silver[1]

BY DAVID GARVIN

RECEIVED DECEMBER 11, 1953

Both the efficient decomposition of ozone by silver (and silver oxide)[2] and the reduction of silver oxide by carbon monoxide are well known.[3] We have observed that carbon dioxide is produced during the decomposition of ozone in mixtures of CO, O_3, O_2 and N_2 upon passage through beds of ascarite, potassium hydroxide or precipitated silver.[4] Of these, only silver is capable of producing as much as one CO_2 molecule per ozone molecule decomposed.

The figure summarizes some experiments with various CO, O_3, O_2, N_2 mixtures on precipitated silver at 0° and atmospheric pressure. Contact times ranged from 0.03 to 0.1 second, CO mole fractions from 0.036 to 0.5, and ozone mole fractions from 0.002 to 0.02. Carbon monoxide was in excess in all cases, and the ozone was completely decomposed. No carbon dioxide production was observed in the absence of ozone. At room temperature and above the decomposition of ozone was favored over the production of carbon dioxide.

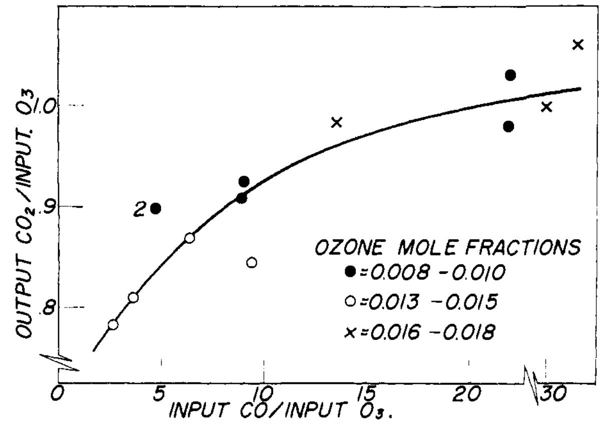

Fig. 1.—Production of carbon dioxide in $CO-O_2-O_3-N_2$ mixtures on precipitated silver.

Empirically the experiments are well correlated by the plot shown, but not by plots of CO_2 or CO_2/O_3 *vs.* CO. The fact that the carbon dioxide produced is limited by the ozone decomposed, and that ozone decomposes completely on silver suggests a primary process such as

$$O_3 + Ag \longrightarrow O\ (\text{bound}) + O_2 \qquad (I)$$

where the surface oxygen may be an oxide or be chemisorbed. The amount of carbon dioxide produced relative to ozone decomposed suggests that competitive processes consume the surface oxygen. One set, consistent with catalytic oxidation of CO, and with our scant knowledge of the ozone decomposition on silver, is

$$O_3 + O\ (\text{bound}) \longrightarrow Ag + 2O_2 \qquad (II)$$

$$CO + O\ (\text{bound}) \longrightarrow Ag + CO_2 \qquad (III)$$

When the data are analyzed according to this mechanism, they indicate that k_2 and k_3 are of the same magnitude.

These arguments indicate a close relation between this rapid, low temperature oxidation and that of CO on silver at higher temperatures. In the latter, a higher temperature (100° or more) is required for the rate of activated adsorption of O_2 to be appreciable. In the former, ozone serves as an efficient source of oxygen, permitting subsequent reaction at 0°. Thus, this work indicates the correctness of Benton's[5] conclusion that the activated adsorption of oxygen is the slow step in CO oxidation on silver.

---

[1] This research was supported by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

[2] W. Manchot and W. Kampschulte, *Ber.*, **40**, 2891 (1907); J. W. Strutt, *Proc. Roy. Soc.* (*London*), **87**, 302 (1912).

[3] See, for example, H. A. J. Pieters, *Chem. Weekblad*, **28**, 250 (1931); S. M. Fainshten, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 37 (1947); M. Katz, "Advances in Catalysis," Vol. V, Academic Press, Inc., New York, N. Y., 1953, pp. 177–216.

[4] S. Dondes, A. J. Hogan, P. Harteck and H. M. Clark, Report SO-3251 (Chemistry) Rensselaer Polytechnic Institute, March, 1953, have recently reported carbon dioxide production on silver foil in the presence of ozone.

[5] A. F. Benton and R. T. Bell, THIS JOURNAL, **56**, 501 (1934).

THE JAMES FORRESTAL RESEARCH CENTER
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

The Decomposition of Benzoyl Peroxide in Glacial Acetic Acid

BY MATTHEW T. GLADSTONE[1]

RECEIVED OCTOBER 15, 1953

Acetyl peroxide, when decomposed in glacial acetic acid, gives a high yield of succinic acid.[2] Kharasch, Jensen and Urry,[3] however, found that no succinic acid is formed when benzoyl peroxide is slowly added to boiling acetic acid. Gelissen and Hermans[4] used a somewhat different technique. They added benzoyl peroxide to acetic acid and the whole was heated for 5 hours at about 90°. They isolated biphenyl, benzene, phenyl benzoate, benzoic acid and *p*-phenylbenzoic acid, but the main product was a resinous mass soluble in alkali.

---

[1] Technical Department, Behr-Manning Corp., Troy, N. Y.

[2] M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, **65**, 15 (1943).

[3] M. S. Kharasch, E. V. Jensen and W. Urry, *J. Org. Chem.*, **10**, 386 (1945).

[4] H. Gelissen and P. H. Hermans, *Ber.*, **58**, 770 (1925).