catalytic activity than palladium, but this criterion provides no basis for explanation of the consistently higher activity of ruthenium. It is possible, of course, that the relatively impure ruthenium may have contained catalytically active impurities or impurities having promoter properties.

In the course of this work, studies on rates of hydrogenation as a function of ratios of catalyst to acceptor were made. The results of these studies are considered elsewhere.[22]

[22] G. W. Watt and M. T. Walling, Jr., *J. Phys. Chem.*, in press.

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[CONTRIBUTION FROM THE NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

Use of Radioactive Iodine to Determine Equilibrium Constants in Ethylene–Iodine-1,2-Diiodoethane Systems

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RECEIVED JUNE 17, 1954

Radioactive iodine has been used to trace the gas phase equilibrium between ethylene, iodine and 1,2-diiodoethane. The results are consistent with those of Cuthbertson and Kistiakowsky and with the lower temperature results of Mooney and Ludlam. The equilibrium data lead to the following molal values for the dissociation of 1,2-diiodoethane at 25°: $\Delta H° = 11.5$ kcal., $\Delta F° = 2.1$ kcal. and $\Delta S° = 31.2$ cal./deg. The entropy of 1,2-diiodoethane at 25°, therefore, must be near 83.2 cal./deg./mole.

Mooney and Ludlam[1] and Cuthbertson and Kistiakowsky[2] have studied the gas phase equilibrium between 1,2-diiodoethane and its dissociation products, namely, ethylene and iodine.[3] The quantitative results of the two teams of investigators agree rather well at low temperatures but disagree at higher temperatures.

Mooney and Ludlam, whose measurements were all made in systems saturated with respect to both iodine and organic iodo compound, found the heat of formation ($\Delta H°$) of 1,2-diiodoethane to be 13.4 kcal./mole at temperatures below 40–45° and 22.3 kcal./mole at temperatures greater than 40–45°. These $\Delta H°$ values were derived from the slopes of logarithmic plots of equilibrium constants against reciprocals of absolute temperatures. The authors considered the figure of 13.4 kcal./mole to be too low because of solid solution formation or because of adsorption of one of the compounds on the surface of the iodine. Cuthbertson and Kistiakowsky studied, at temperatures above 45°, systems in which formation of both solid iodine and solid diiodoethane was avoided. They calculated a heat of formation of diiodo compound of 13.4 kcal./mole and they suggested that Mooney and Ludlam's higher figure of 22.4 kcal./mole was probably in error as a result of some distortion introduced perhaps by solid–solution formation. In an effort to discover which set of equilibrium values and which $\Delta H°$ is correct, we have measured equilibrium constants in 1,2-diiodoethane systems using radioactive iodine to indicate the equilibrium concentrations of both iodine and organic iodo compound.

Experimental

Method.—Radioactive iodine placed in tubes made of 5-mm. glass tubing was cooled and sealed in vacuum. The weight of iodine was determined to the nearest 0.2 mg. The selected procedure does not demand an exact knowledge of this weight. An ampoule containing the active iodine was nicked with a file and was placed in a reaction vessel of capacity in the range 30 to 600 ml. The reaction vessel was evacuated and ethylene was introduced to a pressure judged sufficient to transform half the iodine at equilibrium to diiodoethane. The ethylene was condensed by liquid air and the reaction vessel sealed by means of a flame. Estimates of the change in volume resulting from the presence of the ampoule and from the sealing were applied later as corrections. After allowing the vessel to warm up, the ampoule was broken by shaking the vessel. The amount of iodine was selected so as to avoid saturation with respect to both iodine and iodo compound. Despite these precautions, solids appeared on the vessel surfaces in two experiments. The measurements from these saturated systems were discarded.

After the iodine was released within a reaction vessel, the vessel was thermostated for a period of 12 hours or more, a period of time considerably in excess of what both Cuthbertson and Kistiakowsky and we found necessary to achieve equilibrium. Temperatures were kept within 0.05° of the recorded values in all but a few of the earlier runs in which the range was 0.2°. The preparations thermostatted at 9 and 25° were allowed to stand for several days.

Following the thermostating, the reaction vessels were plunged into a large container of liquid air in order to freeze the system at the composition attained at equilibrium. Active bubbling around the vessels stopped in 10 to 30 seconds depending on the surface to volume ratio. Experiments in which the reaction materials reached equilibrium at the same temperature but in vessels of different sizes and shapes gave results that agreed with each other as well as did duplicate results from experiments in which the vessels were identical. It was concluded that the equilibria were effectively frozen by the treatment described.

The reaction vessels were opened at liquid nitrogen temperatures and 20 ml. of carbon tetrachloride added. Thereafter the temperature was allowed to rise to 0° and the solution of iodine and diiodoethane was acidified with acetic acid and titrated with 0.005 N thiosulfate until the free iodine color was completely discharged. The two layers were separated. To improve the efficiency of the separation, the carbon tetrachloride was washed with two further portions of water and the water layer with two portions of carbon tetrachloride. The water layer containing radioactive iodide ions, together with the washings, was brought to 100 ml. in a volumetric flask. In the same way the carbon tetrachloride layer containing radioactive diiodoethane, together with the appropriate washings, was diluted to 100 ml. The liquids were counted separately.

Counting Procedure.—A special Geiger–Müller counter was prepared with walls about 0.1 to 0.15 mm. thick. The counter fitted into a double-walled jacket designed to contain the radioactive solution (34 ml.) to be counted. The inner wall of the jacket was of the same thickness as the walls of the counter. The jacket carried two arms, one at

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[1] R. B. Mooney and E. B. Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).

[2] G. R. Cuthbertson and G. B. Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

[3] A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

the top and one at the bottom, for use in filling, emptying and washing of the jacket. The Geiger–Müller tube was connected through a preamplifier to a Tracerlab Autoscaler. All samples were counted sufficiently long to reduce the statistical uncertainty in the net rates to 1%.

The counting rates of the active iodine samples were corrected in the standard way[4] for background, counter dead-time and radioactive decay. The corrected counts correspond to definite weights of iodine as determined by the counting of standard samples in carbon tetrachloride and in dilute sodium thiosulfate solution. Within the range of concentrations used, changes in the amount of thiosulfate present in the aqueous layer had no determinable influence on the measured radioactivity.

Materials.—The radioactive iodine in bisulfite solution was received from Oak Ridge National Laboratory in 10-mc. shipments. Each solution containing 10 mc. of active iodine was diluted with a solution containing 5 g. of inactive potassium iodide. Free iodine was recovered from the resulting solutions by adding an excess of 0.1 *N* potassium iodate in the presence of a slight excess of acetic acid. The iodine was desiccated over anhydrous calcium chloride and sublimed three times in an apparatus similar to McCrosky's.[5]

Ethylene, specified by the manufacturer to be 99.5% pure, was passed through a sputtered sodium trap as described by Storch[6] to remove oxygen and was then distilled three times to reduce the content of propane.

Carbon tetrachloride was purified by the method of Fieser.[7]

Results

The principal data on the equilibrium composition of systems in which radioactive iodine was used appear in Table I. In another series of runs, concentrations were secured by titration of inactive iodine. The resulting equilibrium constants while agreeing with the results in Table I were judged to be of inferior accuracy and they do not appear in the table.

TABLE I

EQUILIBRIUM CONSTANTS IN SYSTEMS OF ETHYLENE, IODINE AND 1,2-DIIODOETHANE OBTAINED BY COUNTING RADIOACTIVE IODINE AND IODO COMPOUND

	Equilibrium pressures, mm.			
T, °K.	C_2H_4	I_2	$C_2H_4I_2$	Kp(mm.)
282.1	6.95	0.0380	0.0419[a]	6.3
298.1	15.8	.1379	.1045	20.8
298.1	17.1	.1317	.0978	23.0
308.3	53.1	.1522	.1967	41.1
308.3	53.5	.1410	.1842	41.0
316.1	60.2	.766	.771	59.8
316.1	60.9	.699	.679	62.7
326.3	111.6	.608	.594	114.2
326.3	115.6	.707	.714	114.5
336.0	224.2	1.135	1.330	191.3
336.0	215.7	1.443	1.644	189.3
346.1	313.7	2.188	2.050	334.8
358.6	701.1	1.640	2.001	574.6
358.6	653.9	1.324	1.605	539.4
369.9	817.5	26.93	23.68	929.7
369.9	1017.0	21.65	24.33	905.0
369.9	1007.0	21.58	23.12	939.9
369.9	1019.4	19.77	21.48	938.2

[a] Vapor pressure of solid $C_2H_4I_2$ extrapolated from data of Mooney and Ludlam. System apparently saturated with respect to compound. Activity of compound corresponded to pressure of 0.0729 mm.

When equilibrium constants from the table are plotted in the same diagram with the constants reported by Cuthbertson and Kistiakowsky[2] and by Mooney and Ludlam[1] for temperatures below 40–45°, rather good concordance is found.

The following expression was fitted by least-squares method to the data given in Table I

$$\log_{10}K_p(\text{atm.}) = \frac{-11{,}500}{4.58T} + 6.88 \qquad (1)$$

$\Delta H°$ for the dissociation of 1,2-diiodoethane as recorded in the equation is 11.5 (±0.2) kcal./mole.

Discussion

Two uncertainties arise in making comparison of equilibrium constants from Table I with others. First the constants in Table I represent the distribution of I^{131} between free and bound states rather than the distribution of inactive I^{127}. Second the distribution may be affected by the presence of radiation coming from I^{131}.

The influence of isotopes on the rates of reactions and on equilibria[8] has received much attention. Equilibrium effects are greatest with hydrogen isotopes (100% mass difference). They are very appreciable with carbon and nitrogen isotopes (8% mass difference) but are expected to be inconsiderable with heavier elements.[9] Were sufficient spectroscopic data available, partition functions might be calculated and exact differences in equilibrium estimated.[10] In the absence of these partition functions, we may suppose equilibrium constants with I^{131} and I^{127} to agree to about 1%.

When radiant energy selectively activates just one component in an equilibrium system, large shifts in steady state concentrations may occur.[11] When the radiant energy is absorbed by all the components, equilibrium shifts are smaller although often of considerable magnitude. Water, for example, decomposes extensively under the influence of α-particle bombardment,[12] but less extensively under the influence of fast electrons,[13] and still less under the influence of X-rays.[14] We may expect the moderately energetic β-rays and γ-rays[15] of I^{131} at the low intensity encountered in the present experiments to have only a slight effect on the 1,2-diiodoethane equilibrium, particularly in the gas phase. The following rough calculation supports this conclusion. Not more than 4 μc. of I^{131} (based on activity of sample when shipped from Oak Ridge) was introduced in the equilibrium complexes. If all the β-energy of the I^{131} be dissipated in the gas (an over-estimate) and if 32 e.v. represent the energy to create an ion-pair in the gas, about 7×10^{13} ion-pairs would be formed in the gas

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(4) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 7, 191, 193.

(5) C. R. McCrosky, THIS JOURNAL, **40**, 1662 (1918).

(6) H. H. Storch, *ibid.*, **56**, 374 (1934).

(7) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 365.

(8) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

(9) D. W. Stewart, *Ann. Rev. Phys. Chem.*, **2**, 71 (1951).

(10) H. G. Thode, *ibid.*, **4**, 111 (1953).

(11) G. B. Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., New York, N. Y., 1928, p. 58.

(12) T. Giesel, *Ber.*, **36**, 342 (1903); W. Duane and O. Scheuer, *Compt. rend.*, **156**, 466 (1913).

(13) A. O. Allen, *J. Phys. Chem.*, **52**, 479 (1948).

(14) O. Risse, *Z. physik. Chem.*, **140**, 133 (1929); H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

(15) Landolt–Börnstein, "Zahlenwerte und Funktionen," Springer, Berlin, 6th Ed., Vol. I, part 5, 1952, p. 213.

in 12 hours. This number is about one millionth the number of all the molecules present and of course an even smaller fraction of the number of molecules reacting in 12 hours. One may infer that the radiation from a few microcuries of I^{131} will have a negligible effect in shifting the diiodoethane equilibrium. Viewed differently, the calculation above shows also that the Xe^{131} resulting from the I^{131} decay never contributes appreciably to the pressure of the system nor do possible products of radiation-induced decomposition of ethylene. A direct comparison of the data in Table I with the results of earlier investigators, therefore, seems proper.

One may check the $\Delta H°$ values obtained from equilibrium studies with those derived from thermochemical data. Depending on which data form the basis of the calculations, $\Delta H°$'s ranging from 11.6 to 20.4 kcal./mole may be calculated. The lower figure is obtained if one chooses what seem to be the best available data for (1) the heat of combustion of solid 1,2-diiodoethane (only one value is available, namely, 324.8 kcal./mole reported by Berthelot),[16] (2) the heat of sublimation of iodine (Giauque's figure[17] of 14.88 kcal./mole was chosen), (3) the heat of sublimation of diiodoethane (the only published value is Mooney and Ludlam's,[1] namely, 15.7 kcal./mole) and (4) the heat of combustion of ethylene (the best among the rather discrepant values seems to be the Bureau of Standards' result,[18] *viz*, 337.2 kcal./mole). The agreement between the $\Delta H°$ based on the best available thermochemical data and the $\Delta H°$ found in the present equilibrium study seems better than would have been expected.

The equilibrium constant at 25° computed from equation 1 is equivalent to a $\Delta F°$ value at 25° of 2.1 kcal./mole. By combining this result with $\Delta H°$ in the usual way, *viz.*, through the relation

$$\Delta F° = \Delta H° - T\,\Delta S°$$

one estimates for $\Delta S°$ a magnitude of 31.2 cal./deg./mole. $\Delta S°$ is the difference between the entropy of a mole of gaseous 1,2-diiodoethane and the sum of the entropies of a mole of iodine and a mole of ethylene all at 25° and 1 atm. The latter two molal entropies are 62.29 for iodine[19] and 52.45 for ethylene.[20] Using these entropy values, we find the entropy of a mole of 1,2-diiodoethane to be 83.2 cal./deg. This figure conforms well to the entropies estimated for the corresponding chlorine and bromine compounds[21] as shown in Table II. The figure 83.2 entropy units agrees well also with the molal entropy value of 83 cal./deg. computed statistically.[22]

TABLE II

STANDARD MOLAL ENTROPIES OF DIHALOETHANES AT 25°, CAL./DEG.

1,2-Dichloroethane[21]	73.9
1,2-Dibromethane	78.8
1,2-Diiodoethane[a]	83.2
1,2-Diiodoethane[b]	77.3

[a] Present work. [b] From an equation for K_p derived by Cuthbertson and Kistiakowsky from a combination of their own data with the data of Mooney and Ludlam.

Acknowledgment.—The authors are grateful to Dr. Richard M. Noyes for help in the design of the G. M. counting tube.

NEW YORK, N. Y.

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[19] G. M. Murphy, *J. Chem. Phys.*, **4**, 434 (1936).

[20] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffee, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952, p. 120.

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[22] A. Abrams and T. W. Davis, forthcoming publication.

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Some Vanadyl Complexes with β-Diketones

BY MARK M. JONES

RECEIVED JULY 1, 1954

The preparation and properties of a number of complexes between the vanadyl ion and β-diketones are described. These substances are shown to fall into two groups, one of which apparently shows five coördinated vanadium(IV), and one of which shows six coördinated vanadium(IV). The reactions of the five coördinated compounds with bases to give compounds in which the central vanadium has a coördination number of six are dependent upon both the strength of the base and the presence of favorable stereochemical factors.

Although vanadyl complexes with acetylacetone and benzoylacetone have been known for several decades,[1,2] there have been no detailed descriptions of their reactions nor information on the type of diketone which may be used to form such complexes. The purpose of the present work is to provide information on both of these subjects. Several complexes have been prepared and their substitution reactions studied.

The common methods of preparing vanadyl acetylacetonate yield a turquoise blue solid which has been formulated as $VO(C_5H_7O_2)_2$[1] or $VO(C_5H_7O_2)_2 \cdot H_2O$.[2] The analysis of the product as well as its physical properties[3] support the former composition and would lead to the conclusion that this substance is either polymeric or an example of five coordinated vanadium(IV). The few reactions of this compound which have been studied were formulated by Rosenheim as replacement

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[1] G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, **103**, 78 (1914).

[2] A. Rosenheim and Hsing Yu Mong, *Z. anorg. Chem.*, **148** 34 (1925).

[3] B. P. Block (in a personal communication to Prof. T. Moeller) reports that the properties of vanadyl bis-(acetylacetonate) prepared as reported in this paper are identical with those of the acetylacetonate of vanadium prepared under completely anhydrous conditions.