[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. XIX. Formation Constants of Halogen Complexes from Infrared Measurements[1]

BY ALEXANDER I. POPOV, RAY E. HUMPHREY AND WILLIS B. PERSON

RECEIVED AUGUST 24, 1959

Formation constants of benzene-ICl, dioxane-ICN, metrazole-ICN and pyridine-ICN were determined from the intensities of the infrared absorption bands of these complexes. The values obtained were 0.7 ± 0.2, 1.2 ± 0.4, 15 ± 3 and 51 ± 5, respectively. The formation constant for the first complex compares favorably with the value of 0.54 reported in the literature from measurements in the ultraviolet spectral regions. While it does not seem likely that the use of the infrared spectra of charge-transfer complexes for the determination of formation constants will be, in general, preferred over ultraviolet measurements, still, this research illustrates that in certain cases this method can be quite reliable and useful.

Introduction

Since the work of Benesi and Hildebrand[2] a number of investigations of the formation constants for halogen complexes have been completed using the ultraviolet absorption spectrum of the charge-transfer complex as a measure of the concentration of the complex.[3] Very few such investigations have been made using the infrared absorption spectrum,[4] although there is nothing in principle which prevents such studies. Since the absorption by the complex in the infrared region is very much weaker than it is in the ultraviolet region, the experimental accuracy with which the formation constant can be determined from the studies in the infrared region leaves much to be desired, thus imposing a practical limitation to the usefulness of such studies.

There are occasions when it would be desirable to measure formation constants using the infrared spectrum of the complex. In the course of our studies on the infrared spectra of charge-transfer complexes,[5-7] two such occasions have arisen.[3] The first case occurs when the absorption by the complex is too far out in the ultraviolet region to be studied easily with conventional spectrometers. This is the case with complexes of iodine cyanide. The other question justifying studies of formation constants in the infrared region of the spectrum has been raised by Orgel and Mulliken.[8] They suggest that the weakest charge-transfer complexes are probably not stable complexes in the sense that they are fixed, long-lived chemical entities but that they may be "contact" charge-transfer complexes. They point out that it will be hard to distinguish between these two situations experimentally and that even if measurements in two different spectral regions give the same formation constants, it would not necessarily be a proof of the existence of one definite complex. Only one such comparison has been made previously; Glusker and Thompson[4] obtained a value of 0.7 for the formation constant K_f of the dioxane–iodine complex, from infrared measurements, compared with a value of 0.86 from studies of the ultraviolet and visible spectra.[9,10] It thus seemed worthwhile to investigate another complex in the infrared spectral region.

When we first considered this problem, we had felt that it was important to measure formation constants in different spectral regions for still another reason. It had seemed reasonable to us to believe that the apparent formation constant one would obtain from a mixture of complexes would be weighted according to the molar absorptivities of the different complexes in the spectral region being studied. We had expected that the molar absorptivities of the different geometrical configurations of the complex might have about the same values for the ultraviolet region of the spectrum but that these different configurations would have quite different absorptivities in the infrared region. Thus, we thought that the slight differences reported for the formation constant of the dioxane–iodine complex might be a result of the difference in the weighting of K_f and thus provide some evidence in favor of a mixture of complexes with different geometrical configurations. However, the elegant analysis made by Orgel and Mulliken made it clear that the measured value of K_f was *not* weighted according to absorptivities but that it would be exactly the same when measured in any spectral region. Thus, it seemed clear that the difference in values for the formation constant of dioxane–I_2 must be due to experimental error alone, and we decided to try one more comparison with ultraviolet data.

During our studies of ICl[5] and ICN[6] complexes, we have measured a few formation constants using the absorption of the complex in the infrared region to measure its concentration. From these measurements formation constants could be estimated. Although these are not very accurate, they are of some interest for the reasons cited above.

Experimental Part

The chemicals used in these studies, the experimental difficulties due to reactions and the spectrometer have all been described earlier.[5,6]

---

[1] Presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 14, 1959. This is also paper V of the series "Infrared Spectra of Charge Transfer Complexes."

[2] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[3] See for example the studies by L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 4677, 5039, 5170 (1950); **74**, 640, 4500 (1952); **75**, 3561 (1953).

[4] The only one we know of on halogen complexes is that by D. L. Glusker and H. W. Thompson, *J. Chem. Soc.*, 471 (1955).

[5] W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958).

[6] W. B. Person, R. E. Humphrey and A. I. Popov, *ibid.*, **81**, 273 (1959).

[7] W. B. Person, R. E. Erickson and R. E. Buckles, *ibid.*, **82**, 29 (1960).

[8] L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

[9] J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

[10] L. S. Lilich and O. E. Presnikova, "Nauchnye Zapiski, Leningrad. Gosud. Univ. im. A. A. Zhdanova," No. 163, Ser. Khim. Nauk No. 12, 3 (1953).

Formation constants were determined for the benzene–ICl, dioxane–ICN, metrazole–ICN and pyridine–ICN complexes. (Metrazole is the pentamethylenetetrazole of ref. 5.)

For the benzene–ICl complex, solutions of 0.1 *M* ICl were prepared in carbon tetrachloride and with benzene concentrations of 0.5, 1.0, 1.5 and 2.0 *M*. For each solution the spectrum of the I–Cl stretching fundamental at 355 cm.$^{-1}$ in the complex was obtained using the fastest rate of scan available for the spectrometer in order to minimize the reaction between ICl and benzene (or cell windows). In order to avoid investing more time in the experiment than the results would justify, the apparent absorbance [log $(T^0/T)_\nu$] was used to determine concentration instead of the integrated area. This procedure is justified in the Discussion. The results at two different wave lengths are given in Table I together with the calculation of the formation constant by the Scott modification[11] of the Benesi–Hildebrand equation

$$\frac{A \cdot b \cdot D}{A_s} = \frac{1}{K_f \cdot a_m} + \frac{D}{a_m}$$

TABLE I

DATA FOR BENESI–HILDRBRAND–SCOTT EQUATION FOR DETERMINATION OF BENZENE–ICl FORMATION CONSTANT

Benzene concn., *M*	A_s 355 cm.$^{-1}$	X^a 355 cm.$^{-1}$	A_s 357 cm.$^{-1}$	X^a 357 cm.$^{-1}$
0.5	0.200	0.250	0.220	0.228
1.0	.300	.333	.330	.300
1.5	.380	.395	.420	.359
2.0	.400	.500	.450	.444
2.5	.480	.520	.520	.480
$K_f{}^b$	0.72		0.75	
$a_m{}^c$	7.5		7.8	

^{a} X = (Bz)·*b*·(ICl)/A_s. The path length is expressed in mm. ^{b} The concentration of ICl was 0.1 *M* in all solutions. ^{c} The units of molar absorptivity are l. moles^{-1} mm.$^{-1}$.

TABLE II

DATA FOR BENESI–HILDEBRAND–SCOTT EQUATION FOR DETERMINATION OF DIOXANE–ICN FORMATION CONSTANT

Dioxane concn., *M*	A_s 469 cm.$^{-1}$	X^a 469 cm.$^{-1}$	A_s 460 cm.$^{-1}$	X^a 460 cm.$^{-1}$
0.4	0.245	0.163	0.110	0.365
.6	.320	.188	.170	.354
.8	.360	.222	.180	.445
1.0	.400	.250	.225	.444
1.2	.420	.286	.230	.522
1.4	.440	.319	.250	.560
$K_f{}^b$	1.55		0.90	
$a_m{}^c$	6.5		4.0	

^{a} X = (Diox)·*b*·(ICN)/A_s. The path length is expressed in mm. ^{b} The concentration of ICN was 0.1 *M* in all solutions. ^{c} The units of molar absorptivity are l. moles^{-1} mm.$^{-1}$.

where *A* is the initial molar concentration of the acceptor, *D* is the initial molar concentration of the donor, *b* is the cell length, A_s the absorbance of the complex, K_f the formation constant for the complex (concentration units are moles/l.) and a_m is the molar absorptivity at this frequency. If the left-hand side of this equation is plotted against *D*, a straight line is obtained with a slope of $1/a_m$ and an intercept of $1/K_f a_m$. Some estimate of the error can be obtained by carrying out the calculations at different wave numbers. In order to illustrate the reliability of this method, *using infrared data*, we show the Benesi–Hildebrand–Scott plots for the benzene–ICl complex in Fig. 1. This figure shows that this method can be applied in the infrared region of the spectrum, with proper precautions, to give data which are not too much different from those obtained using ultraviolet spectra. The resulting formation constant is given in Table V.

For the dioxane–ICN system, two absorption bands are found in the I–C stretching region.[6] In studying the formation constant, we have assumed that the stronger band at 469 cm.$^{-1}$ was due to the one-to-one dioxane–ICN complex and the formation constant was calculated by the Benesi–Hildebrand–Scott procedure outlined above. Various concentrations of dioxane were used with a 0.1 *M* solution of iodine cyanide in chloroform. Values used in calculating K_f from data at two different wave numbers are presented in Table II. The plots show a relatively minor scatter similar to that in Fig. 1.

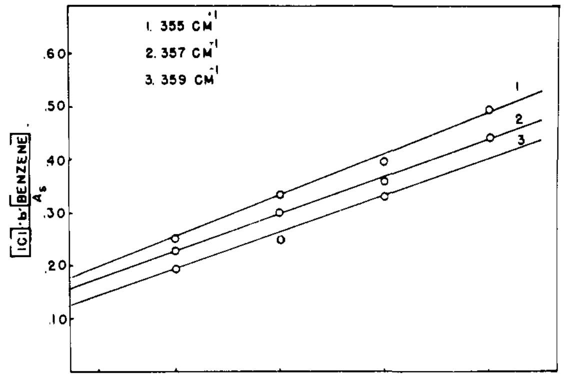

Fig. 1.—Benesi–Hildebrand–Scott plot for the benzene–ICl complex.

For the metrazole–ICN complex, the Benesi–Hildebrand–Scott assumption that the complex be weak is not valid and the procedure was therefore modified. We tried to use the spectrum to determine directly the equilibrium values of the concentrations, which then were used to evaluate K_f. The concentration of the complex was determined using a calibration curve and the absorbance of the complex. The calibration curve was constructed by measuring the absorbances of varying concentrations of ICN in a solution of 1 *M* metrazole in benzene. The ICN concentrations were chosen so that the assumption that all the ICN was complexed would be valid. The resulting Beer's law plots at different wave numbers are shown in Fig. 2. Using this calibration curve, the concentration of the complex could be determined in an unknown mixture. Knowing the initial concentrations of ICN and metrazole, we could then easily calculate the equilibrium concentrations and thus the formation constant. The results for several solutions are shown in Table III.

TABLE III

DATA ON DETERMINATION OF THE FORMATION CONSTANT OF THE METRAZOLE-ICN COMPLEX

Concn. moles/l. Orig. met.	Concn. moles/l. Complex	Concn. moles/l. Free ICN	Concn. moles/l. Free met.	A_s	K_f
		450 cm.$^{-1}$			
0.050	0.023	0.077	0.027	0.090	10
.075	.030	.064	.039	.140	14
.100	.043	.057	.057	.170	13
.125	.051	.049	.074	.200	14
.150	.062	.038	.088	.240	18
.175	.066	.034	.109	.250	18
				Av. K_f	15
		442 cm.$^{-1}$			
0.050	0.025	0.075	0.025	0.070	13
.075	.030	.070	.045	.085	9
.100	.043	.057	.057	.120	13
.125	.053	.047	.072	.150	16
.150	.062	.038	.088	.180	19
.175	.068	.032	.107	.190	20
				Av. K_f	15

The determination of K_f for the pyridine–ICN complex was carried out in the same way as for the metrazole complex. The Beer's law calibration is similar to Fig. 2 and the results for several solutions are given in Table IV.

---

(11) R. L. Scott, *Rec. trav. chim.*, **75**, 787 (1956).

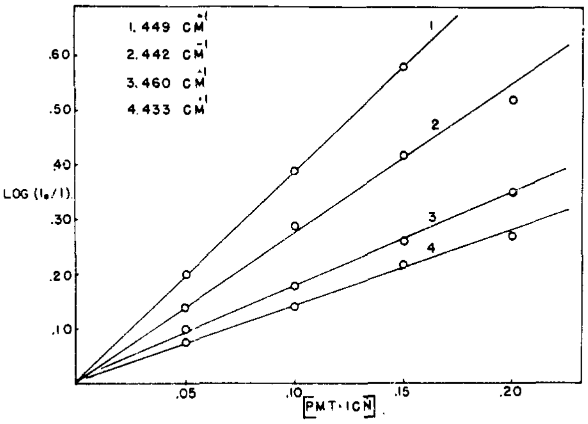

Fig. 2.—Beer's law plot for metrazole–ICN complex in benzene.

The formation constants thus determined are presented in Table V. An attempt has been made in each case to determine the range of K_f due to the uncertainty in the experimental data. These are also indicated in the table.

TABLE IV

DATA ON DETERMINATION OF THE FORMATION CONSTANT OF PYRIDINE–ICN COMPLEX

Concn., moles/l.					
Orig. Py	Complex	Free ICN	Free Py	A_s	K_f
		445 cm.$^{-1}$			
0.075	0.054	0.046	0.021	0.125	56
.100	.065	.035	.035	.150	53
.120	.071	.029	.049	.165	47
				Av. K_f	52
		430 cm.$^{-1}$			
0.075	0.054	0.046	0.021	0.245	56
.100	.064	.036	.036	.290	62
.120	.071	.029	.049	.320	47
				Av. K_f	55
		424 cm.$^{-1}$			
0.075	0.053	0.047	0.022	0.335	49
.100	.060	.040	.040	.385	48
.120	.067	.033	.053	.430	40
				Av. K_f	46

TABLE V

FORMATION CONSTANTS

Complex	K_f[a]	K_f[b]
Benzene–ICl	0.7 ± 0.2	0.54
Dioxane–ICN	1.2 ± 0.4	
Metrazole–ICN	15 ± 3	
Pyridine–ICN	51 ± 5	

[a] This work. Concentration in moles/l. [b] From measurements in the ultraviolet region. Ref. 3.

Discussion

From the scatter of the results in the tables, it would seem that the uncertainty in the formation constants is not unreasonable. Certainly the order of magnitude is well established. Some improvement in accuracy could be attained if more care were taken in measuring initial concentrations, etc., but not without a much greater investment in time.

We realize that the use of absorbance, rather than integrated absorption, as a measure of concentration can be criticized. However, we feel that this procedure is justified for the following reasons. Experimentally, the plots shown in Fig. 2 show that Beer's law is obeyed quite well for this absorption band. The reason for this can be seen when we realize that the apparent half-intensity widths, $\Delta\nu_{1/2}^a$, for these bands are large (~15 cm.$^{-1}$)[5,6] and the spectral slit width s of the spectrometer is relatively small (~3 cm.$^{-1}$). Thus the ratio $\Delta\nu_{1/2}^a/s$ is greater than five for all these measurements. If we refer to Ramsay's paper[12] for the effect of resolution on the band shape, we find that even though the apparent absorbance, log (T_0/T), is not equal to the true absorbance log (I_0/I), the correction factor is very close to 1.00 (about 1.02) and *furthermore it is constant as log (T_0/T) changes.* Thus, when $\Delta\nu_{1/2}^a/s$ is this large we may expect Beer's law to hold when absorbance is plotted against concentration.

The values for the formation constants of the ICN complexes in Table V are considerably smaller than the corresponding values for ICl complexes,[3,13] as would be expected for this weak acceptor.

Perhaps the most important result is the comparison between the value of K_f for the benzene–ICl complex measured in the infrared region and the value measured in the ultraviolet region of the spectrum. Although our value of 0.7 is somewhat higher than the value of 0.54 reported by Keefer and Andrews,[3] we believe the agreement between the two numbers is within the experimental error. In fact, there is quite a difference between the concentration of the solutions we have studied and the concentration of the solutions used by Keefer and Andrews; there could thus be some difference expected due to the change in the activity coefficients. However, we conclude that these constants are the same, as predicted by the equations of Orgel and Mulliken.[8] It should be emphasized that these results do not necessarily validate Orgel and Mulliken's assumption as to the existence of "contact charge-transfer" complexes. While it is true that the Benesi–Hildebrand–Scott treatment of experimental data does not present a distinction between one complex of definite geometric configuration and a multiplicity of complexes of different configurations, nevertheless, it seems that other experimental evidence[5,6] supports the idea that there is no fundamental difference between the strong and weak halogen complexes.

Acknowledgments.—Partial financial support from the Office of Ordnance Research, U. S. Army, and from the Institute of Neurological Diseases and Blindness, P.H.S. (grant B-1095), is gratefully acknowledged. R.E.H. wishes to thank the Graduate College of the State University of Iowa for a research assistantship, and the Eastman Kodak Company for a predoctoral fellowship.

IOWA CITY, IOWA

---

[12] D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

[13] A. I. Popov, C. Castellani-Bisi and M. Craft, *ibid.*, **80**, 5346 (1958).