position of silver carbonate. The elimination by Garner and Reeves of this maximum rate using annealed silver oxide probably was due to the extremely large reduction in surface area of the oxide during the annealing. The larger particles (diameter $\sim$0.8 mm.) would have formed much less silver carbonate than the finely divided powder of the original preparation. The diameter of the particles of our preparation B, which was similar to Garner's, was $\sim 4.0 \times 10^{-3}$ mm. The reported sensitivity of silver oxide to light presumably was due to the presence of silver carbonate.

The pressure–time plots of Hood and Murphy, while not covering the complete decomposition, resemble those shown here. Pressure measurements were carried out with a differential water manometer, the evolved CO_2 thus largely dissolving in the water.

The acceleratory stage of the decomposition is fitted by a square-root plot as opposed to the cube-root plot applied by Garner and Reeves.[6] The square-root relationship indicates two-dimensional growth of a fixed number of nuclei. In a precipitated solid, such as specimen C, the density of dislocations will be high. A number of these, especially after annealing at 280° for 3 hr., would be concentrated in sub-boundaries. During decomposition two-dimentional growth of the nuclei would possibly occur along such boundaries. The negative intercept on the abscissa of the plot of $P^{1/2}$ against t shows that initially the growth of the nuclei is abnormally fast. The discrepancy between our findings and those of Garner and Reeves[6] might be explained by the following observations. The cube-root plot which they applied does not always appear to be linear. In Fig. 1 of their paper the plot of $P^{1/3}$ against t for the decomposition at 315.7° shows a distinct curvature of the line. The same applies to certain of the "split-run" curves in Fig. 3. A photographic enlargement of the plots for the decomposition at 315.7° was made and a straight line was obtained using the square-root relationship.

The activation energy of 28.3 kcal./mole is in reasonable agreement with the value found by Lewis,[1] Hood and Murphy[2] and Averbukh and Chufarov.[5] The estimated accuracy of our result is ± 1.5 kcal./mole.

The acceleratory stage of the decomposition proceeds by a mechanism of non-branching two-dimensional reaction planes and it is to be expected that after interference of the planes the undecomposed silver oxide will consist of isolated blocks of material in which no nuclei are present. In these blocks if each molecule possesses an equal probability for decomposition, then the rate of reaction will be proportional to the amount of substance undecomposed and the unimolecular decay law 6 will apply.

The mechanism suggested for the decomposition of pre-irradiated $KMnO_4$ and $AgMnO_4$ involves the annealing of point defects and the accumulation of strain in the crystal over the induction period. The strain results in cracking or fracturing of the solid and reaction occurs in these new reactive surfaces by a branching chain mechanism. The absence of any similar observable effect with pre-irradiated silver oxide may be associated with the fact, as shown by grinding, that the creation of new surfaces does not increase the rate of reaction. As well, it is possible that annealing of the point defects may not occur at the decomposition temperature. Silver oxide is a covalent compound and in such compounds defects appear to be very stable. For example, heating irradiated (fast neutrons) quartz at 100° for three weeks produces no observable recovery of the thermal conductivity change, and heating well above the α-β transition point (573°) is required before any major recovery occurs.[11]

The authors wish to thank the C.S.I.R. (S.A.) for a grant to cover the cost of irradiations and African Explosives and Chemical Industries for a scholarship held by P.J.H.

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(11) R. Berman, P. G. Klemens, F. E. Simon and T. M. Fry, *Nature*, **166**, 864 (1950); R. Berman, *Proc. Roy. Soc.* (*London*), **A208**, 90 (1951).

[CONTRIBUTION FROM THE LABORATORY OF CHEMICAL SPECTROSCOPY, TOKYO INSTITUTE OF TECHNOLOGY]

The Molecular Complexes between Iodine and Various Oxygen-Containing Organic Compounds

BY HARUKA YAMADA AND KUNIO KOZIMA

RECEIVED JULY 10, 1959

When iodine was added to solutions of various oxygen-containing organic compounds, shifts of the infrared absorption bands and changes in the intensities of the bands were observed. These shifts may indicate the formation of complexes between iodine and the solutes. In the case of the ketone–iodine complexes, the intensities of the bands assigned to the C=O stretching vibrations of the ketones increased remarkably, while in the case of the ethyl ether–iodine complex, the intensity of the band assigned to one of the C–O stretching vibrations of ethyl ether decreased. The charge-transfer from the oxygen atoms to iodine molecules and the change in the ionicity of the donating groups, caused by the transfer, may account for most of these phenomena. Although methyl acetate and 3-phenylsydnone possess two or more atoms having lone-pair or π-electrons, iodine combines only with the carbonyl group. For each system the formation constant of the 1:1 complex was determined.

It is well known that molecular complexes are formed between iodine and various organic compounds having lone-pair or π-electrons.[1,2] The bond between them may be due mainly to a charge-transfer force. Although the existence of the molecular complexes frequently is detected by the

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(1) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); *ibid.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(2) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954); S. P. McGlynn, *ibid.*, **58**, 1113 (1958).

charge-transfer spectra in the ultraviolet or visible region, infrared absorption measurements can also shed light on the nature of these molecular complexes.

When iodine is added to various organic compounds[3–5] relatively large shifts are observed in the frequencies of the infrared absorption bands associated with the vibrations of the functional group behaving as an electron donor. Since the intensities of infrared absorption bands are related to bond moments, the intensity measurements of these bands will afford knowledge of the polarity of the molecular complexes. The formation constants of the complexes can also be determined from the intensity measurements. This is an effective method even for a system, such as acetone–iodine, in which the charge-transfer spectrum is hardly detectable in the ultraviolet region.

With these objects in mind, we undertook this study of the complexes which are formed between iodine and various oxygen-containing organic compounds.

Experimental

The infrared spectra were measured with a Perkin-Elmer Model 112 Infrared Spectrophotometer equipped with CaF_2, NaCl and KBr prisms. A 0.1 mm. KBr fixed cell and a KBr demountable cell were used. The thickness of the former was determined by the interference method.

Iodine was purified by sublimation with calcium oxide and potassium iodide. Carbon disulfide was used as the solvent for the dilute solution because iodine dissolves in it readily and solvation does not occur. Both solutes and solvents were purified by fractional distillation and only that fraction was used which distills at constant temperature.

Pure 3-phenylsydnone (m.p. 135°) was prepared by the method of Hashimoto and Ohta.[6]

The intensity measurements were made for the dilute solution with a constant slit width and a background trace of the pure solvent was run so that it was superimposed. The concentrations of the dilute solutions both for iodine and another solute ranged from 0.05 to 1 mole per liter. A point-by-point measurement of the absorbance, $\log (I_0/I)$, was made from the chart. The absorbances were plotted against the wave numbers, and the half-width of the band was determined from the curve. The integrated absorption intensity A (mole^{-1}-l.-cm.$^{-2}$) is calculated by equation 1

$$A = \frac{\pi}{2}\frac{1}{Ct}\Delta\nu_{1/2}\ln (I_0/I)_{\nu(\max)} \qquad (1)$$

where C is the concentration of the compound in moles per liter, t the thickness of the cell in cm., $\ln (I_0/I)_{\nu(\max)}$ the value of $\ln (I_0/I)$ at the absorption maximum and $\Delta\nu_{1/2}$ the half-width in cm.$^{-1}$. By a proper choice of prisms, thickness and concentration of the solutions, it was possible to neglect the corrections for the finite slit width.[7]

Results and Discussion

(1) **Ketone–Iodine Complexes.**—It is well known that the C=O stretching band of acetone shifts to lower frequency upon formation of the acetone–iodine complex.[3–5,8] In the present work, we measured the infrared spectrum of a carbon disulfide solution of acetone to which iodine was added and found that several bands of acetone change in frequency or in intensity on formation of the complex. The frequency shifts, which are given in Table I, are qualitatively similar to the results reported for the acetone–lithium perchlorate complex by Pullin and Pollock.[9]

TABLE I

FREQUENCY AND INTENSITY OF BANDS OF ACETONE AND ACETONE–IODINE COMPLEX

Band		$\nu_{\max}$ (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$A \times 10^{-4}$	K (l./mole) at ~30°
Overtone of	Acetone	3416			
C=O stretch	Complex	3384			
C=O stretch[a]	Acetone	1716	12.0	1.36	
	Complex[b]	1700	16.0	7.5	0.29
	Complex[c]	1701	16.0	8.2	.27
C—C=O	Acetone	529.3	9.0	0.192	
bend.[a]	Complex[d]	534.0	11.6	.14	.29
C–C–C anti-	Acetone	1216	9.9	.61	
sym. stretch[a]	Complex[e]	1223	10.0	1.1	.32

[a] Ref. 10. [b] Initial concn. in mole/l.: acetone, 0.146; iodine, 0.347; complex, 0.013. [c] Initial concn. in mole/l.: acetone, 0.0768; iodine, 0.364; complex, 0.0068. [d] Initial concn. in mole/l.: acetone, 0.980; iodine, 0.264; complex, 0.184. [e] Initial concn. in mole/l.: acetone, 0.0916; iodine, 0.204; complex, 0.0055.

The intensities of the bands at 789 and at 892 cm.$^{-1}$ decrease, although the band maxima do not shift. According to Miyazawa[10] the 789 cm.$^{-1}$ band is associated with the C–C–C symmetric stretching vibration. The 892 cm.$^{-1}$ band may be due to the methyl rocking vibration.

The absorption curve of the C=O stretching band for the solution is shown in Fig. 1. The unbroken line represents the experimental curve and the broken lines represent the two Lorentz curves having their maxima at 1716 (free acetone) and at 1701 cm.$^{-1}$ (complex), respectively. These curves are drawn so that their sum coincides with the experimental curve. The area intensity of the right band is equal to $A(C_1 - x)t$, in which A is the integrated absorption intensity (see equation 1) of the C=O band of free acetone, C_1 the initial concentration of acetone, x the concentration of the complex and t has the same meaning as equation 1. The value of x was determined by this area intensity. By use of the area intensity of the left band and the value of x, the integrated absorption intensity of the C=O band of acetone in the complex was determined. The results thus obtained are included in Table I. The formation constant K for the complex at 30° was calculated by

$$K = \frac{x}{(C_1 - x)(C_2 - x)} \qquad (2)$$

where C_2 is the initial concentration of iodine. We consider both our results of x (see footnotes b and c of Table I) and K to be accurate within about 5%. The formation constant in solution should be expressed in terms of the activities of the solutes. In the present case, however, concentrations instead of activities could be used since the measurements were made on dilute solution in a non-polar solvent. The fact that the formation constants

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(3) D. L. Glusker, H. W. Thompson and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1407 (1954).

(4) D. L. Glusker and H. W. Thompson, *J. Chem. Soc.*, 471 (1955).

(5) R. N. Haszeldine, *ibid.*, 4145 (1954).

(6) M. Hashimoto and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (Nippon Kagaku Zasshi), **78**, 181 (1957).

(7) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

(8) J. Morcillo and J. Heranz, *Anales real soc. espan. fis. y quim.* (Madrid), **50B**, 117 (1954); *Chem. Abst.*, **48**, 8655 (1954).

(9) A. D. E. Pullin and J. M. Pollock, *Trans. Faraday Soc.*, **53**, 11 (1958).

(10) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (Nippon Kagaku Zasshi), **74**, 915 (1953).

obtained for solutions of various concentrations are in agreement indicates the formation of the 1:1 complex. The C=O stretching band increases remarkably in intensity on formation of the complex.

The results for the bands assigned to the C—C=O bending vibration and the C–C–C antisymmetric stretching vibration are included in Table I. The method for obtaining the results is the same in the case of the C=O stretching band. On formation of the complex both bands shift to larger frequencies. Since the changes in both frequency and intensity for these bands are smaller than those for the C=O stretching band, the results obtained are less accurate than those for the C=O stretching band. Nevertheless, the values of the formation constant obtained by analyzing these bands are in agreement with the values obtained from the C=O band.

Although Glusker and Thompson[4] in their infrared studies were unable to detect the cyclohexanone–iodine complex because of iodination, we found this complex in a solution prepared by mixing dilute carbon disulfide solutions of cyclohexanone (*e.g.* 0.4 mole/l.) and iodine (*e.g.* 0.4 mole/l.). The infrared spectrum of the complex is similar in remarkable points to that of the acetone–iodine complex. The results are given in Table II, together with tentative assignments of the bands.

TABLE II

FREQUENCY SHIFTS CAUSED BY CYCLOHEXANONE–IODINE COMPLEX FORMATION

Wave number of free cyclohexanone band (cm.$^{-1}$)	Wave number of cyclohexanone–iodine complex band (cm.$^{-1}$)	Assignment
3412	3389	Overtone of C=O stretch
1715	1698	C=O stretching
969	966	C—C stretching
749	754	CH_2 rocking
487	493	C—C=O bending

The results obtained by analyzing the C=O stretching bands of the cyclohexanone–iodine system in dilute solution are shown in Table III. The C=O band increases remarkably in intensity on formation of the complex.

TABLE III

FREQUENCY AND INTENSITY OF THE C=O BAND OF CYCLOHEXANONE AND OF THE CYCLOHEXANONE–IODINE COMPLEX

	Initial concn. (mole/l.)						
	Cyclohexanone	Iodine	Complex (mole/l.)	ν_{max} (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	*A* $\times 10^{-4}$	*K* (l./mole) at ~30°
Free cyclohexanone				1715	13.4	2.43	
Complex	0.1185	0.156	0.0093	1698	20	12.6	0.56

According to the theory proposed by Mulliken,[1] stabilization of ketone–iodine complexes is provided by resonance between a non-bonded structure $>C=O\ I_2$ and a dative structure $>C=O^+—I_2^-$; our results on the infrared spectra of these complexes can be explained in terms of this model.

The form of the normal vibration leading to absorption at about 1715 cm.$^{-1}$ for ketones can be considered approximately as a change, Δr, in the C=O distance. Since vibrational intensities depend not on the molecular moment μ but on its rate of change with normal coördinate or approximately with interatomic distance, $d\mu/dr$, we cannot at present use the values of the intensity *A* to derive quantitative measures of the polar properties of the C=O bond. But the marked increase in *A* of the C=O stretching band on formation of the complex suggests that $d\mu/dr$ for the C=O band is much greater in ketones of the complexes than in free ketones. Furthermore, for such a polar group as C=O, it is highly probable[11] that the increase in $d\mu/dr$ is caused by the increase in the bond moment of the C=O group of ketones.

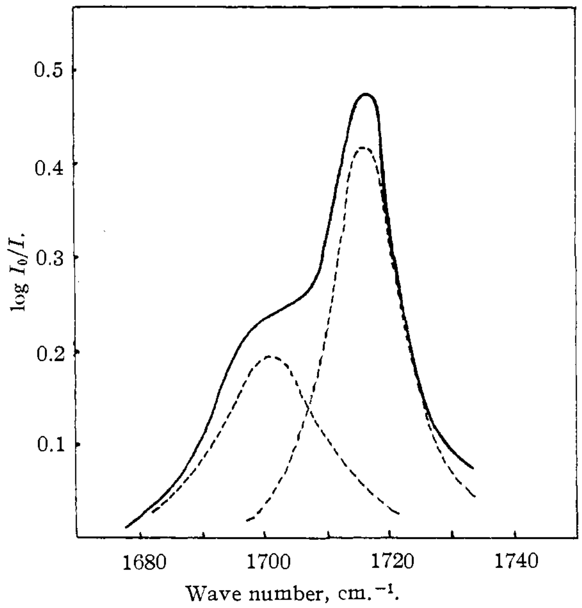

Fig. 1.—The band contour (unbroken line) of the C=O stretching mode of the acetone–iodine solution in CS_2. The band is divided into the band of free acetone (right broken line) and of acetone in the complex (left broken line).

According to the theory based on the molecular orbital treatment, there is good reason to believe that the bond increases with the contribution of the dative structure.

As for unsaturated bonds, an increase in the coulomb integral α_r of atom *r* generally results in a decrease of the π-electron density q_r of the same atom, *i.e.*, $\partial q_r/\partial\alpha_r < 0$.[12] If a lone-pair electron of the oxygen atom of the C=O bond transfers to the iodine molecule, the coulomb integral of the oxygen atom will decrease and, therefore, the π-electron density of the same atom will increase. This increase may account for the increase of the ionicity and the moment of the C=O bond on formation of the complex.

The fact that the frequency of the C=O band shifts to lower frequency due to complex formation indicates a decrease of the C=O stretching force constant and of the C=O bond order. According

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(11) G. M. Barrow (*J. Chem. Phys.*, **21**, 2008 (1953)) has showed that the change in the C=O band intensity of compounds containing conjugated C=O group is due to the availability of a charge-separated electronic configuration.

(12) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947).

to the L.C.A.O. M.O. approximation, the bonding orbital Ψ of the π-electrons of the C=O bond is expressed in the form

$$\Psi = (1 - a^2)^{1/2}\varphi_c + a\varphi_O$$

where φ_C and φ_O are the atomic π-electron orbitals of the atoms C and O, respectively, and a is the coefficient. Since the oxygen atom is more electronegative than the carbon atom, the value of a should be larger than $(1 - a^2)^{1/2}$. As the bond order $p_{C=O}$ is expressed by

$$p_{C=O} = 2a(1 - a^2)^{1/2}$$

the bond order decreases with increasing a, since a is larger than $1/2$. Accordingly, the increase of the π-electron density of the oxygen atom, *i.e.*, the increase of a, results in the decrease of the C=O stretching force constant.

The increase in frequency of the C=O bending vibration may indicate an increase of the C=O bending force constant caused by the attractive force between the oxygen atom and the iodine molecule.

Because of the weak bonding between acetone and iodine, the normal vibrations of the complex may be regarded as the sum of the normal vibration of iodine and those of acetone having slightly different C=O stretching and bending force constants from those of free acetone. The normal vibrations of acetone in the complex were calculated on this basis and the calculated frequency shifts were in accord with those observed. These calculations will be reported in detail in the near future.

The band at 1216 cm.$^{-1}$ assigned to the C–C–C antisymmetric stretching vibration increases in both intensity and frequency upon formation of the complex. The increase in frequency is mainly due to the increase of the C=O bending force constant.

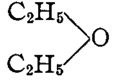
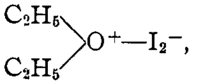
Upon complex formation, the band at 789 cm.$^{-1}$ assigned to the symmetric C–C–C stretching vibration does not seem to shift but decreases in intensity. The former observation can be explained by the fact that the frequency of this band is influenced by the C=O stretching force constant, which decreases, and the C=O bending force constant, which increases; these changes, therefore, cancel each other as far as their effect on the symmetric C–C–C band is concerned.

(2) **Ethyl Ether–Iodine Complex.**—It is known[3–5] that when iodine is added to ethyl ether, the C–O stretching band at 1118 cm.$^{-1}$ shifts to lower frequency and that this shift is due to the formation of the ethyl ether–iodine complex. As the value of this frequency shift and the change in its intensity had not been determined previously, we analyzed this band in detail (see Table IV).

TABLE IV

FREQUENCY AND INTENSITY OF THE C–O BAND OF ETHYL ETHER AND OF THE ETHYL ETHER–IODINE COMPLEX

	Initial concn. (mole/l.) Ether	Initial concn. (mole/l.) Iodine	Complex (mole/l.)	ν_{max} (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	A $\times 10^{-4}$	K (l./mole) at about 30°
Ether				1118	17.3	1.88	
Complex	0.151	0.186	0.012	1097	14	1.2	0.49
	.257	.356	.027	1098	14	1.2	.37
	.242	.321	.028	1098	14	1.2	.45

The decrease in frequency of this band indicates the decrease of the C–O stretching force constant. It seems likely that the decrease in intensity indicates the decrease of the C–O bond moment. If the complex is stabilized by resonance between a non-bonded structure  $(C_2H_5)_2O$ I_2 and a dative structure  $(C_2H_5)_2O^+—I_2^-$, it follows that the decrease of this moment may be caused by the transfer of a lone-pair electron of the oxygen atom to the iodine molecule.

Ham[13] and de Maine[14] have obtained the formation constant for the ethyl ether–iodine solution in *n*-heptane and in carbon tetrachloride, respectively, by measuring the charge-transfer spectrum in the ultraviolet region; our mean value of K at about 30° (0.43 l./mole, see Table IV) expressed in mole fraction is 4.8, which seems to be in accord with Ham's value (at 21.5°) of 4.9 in mole fraction[15] but differs from de Maine's value (extrapolated to 30°) of 7.9 in mole fraction.

The agreement of the K values in Table IV for the various concentrations indicates the formation of the 1:1 complex.

(3) **Methyl Acetate– and 3-Phenylsydnone–Iodine Complexes.**—We wished to determine which oxygen of the ester, the carbonyl and the ether oxygen, behave as the electron donor. When iodine was added to a dilute carbon disulfide solution of methyl acetate, a few spectral changes were observed, which may be ascribed to the formation of a methyl acetate–iodine complex. The results are shown in Table V.

TABLE V

FREQUENCY AND INTENSITY OF BANDS OF METHYL ACETATE AND OF THE METHYL ACETATE–IODINE COMPLEX

	Initial concn. (mole/l.) Methyl acetate	Initial concn. (mole/l.) Iodine	Complex (mole/l.)	ν_{max} (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	A $\times 10^{-4}$	K (l./mole) at ~30°
Overtone of C=O stretching band							
Methyl acetate				3475			
Complex				3461			
C=O stretching band							
Methyl acetate				1749	12.3	2.71	
Complex	0.112	0.374	0.011	1724	27	7.1	0.30
	0.112	0.259	0.010	1724	26	7.1	0.39
C–O stretching band							
Methyl acetate				1241	14.7	2.79	
Complex	0.112	0.374	0.013	1257	17	3	0.36
	0.112	0.259	0.008	1259	19	4	0.31

Since the results obtained for the 1749 cm.$^{-1}$ band, assigned to the C=O stretching vibration, are similar to those obtained for the C=O bands of ketone–iodine complexes, it follows that the iodine molecule adds to the C=O group of the ester.

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(13) J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952).

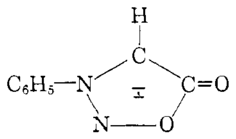
(14) P. A. D. de Maine, *ibid.*, **26**, 1192 (1957).

(15) By extrapolating with de Maine's value of the heat of formation of −4.30 kcal., the value of K at 30° was estimated to be 4.0.

The band at 1241 cm.$^{-1}$, which may be assigned to the C–O stretching vibration according to Glusker, *et al.*,[4] increases in frequency upon complex formation. If the iodine molecule combines directly with the oxygen atom of the C–O bond, the band should decrease in frequency as is the case for the ether–iodine complex. The increase observed may be due to a secondary effect exerted by the neighboring C=O bond. The similarity of the *K* values indicates that the 1:1 complex is formed in this case also. The concentrations of the complex were estimated from the decrease in intensity of the C=O or C–O band of free methyl acetate, as indicated in the table.

If the complex is stabilized by the transfer of a lone-pair electron at the oxygen atom of the C=O group, it is very probable that the first ionization potential of the ester is due to the removal of this lone-pair electron.

Sydnone is a meso-ionic compound with the peculiar structure[16] shown below. As 3-phenylsydnone does not dissolve in non-polar solvents, the measurements were made on an acetonitrile solution. When iodine was added to the solution, the band at 1756 cm.$^{-1}$ assigned to the C=O stretching vibration shifts to 1749 cm.$^{-1}$, and the band at 843 cm.$^{-1}$, assigned to the C–O stretching vibration, shifts to 854 cm.$^{-1}$. These changes are due to the formation of the sydnone–iodine complex with the iodine attached to the oxygen atom of the C=O group, since the shifts are similar to those observed for the ester–iodine complex. No abnormal behavior was observed for the complex in spite of the peculiar structure of sydnone. The results obtained for the intensity of the C=O stretching band and the formation constant at about 30° are shown in Table VI.



3-phenylsydnone

TABLE VI

FREQUENCY AND INTENSITY OF THE C=O BAND OF 3-PHENYLSYDNONE AND OF THE SYDNONE–IODINE COMPLEX

	Initial concn. (mole/l.)		Complex (mole/l.)	ν_{max} (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$A \times 10^{-4}$	*K* (l./mole) at ~30°
	Sydnone	Iodine					
3-Phenyl sydnone				1756	14.8	10.8	
Complex	0.0321	0.150	0.0041	1749	19	14	1.0

From the fact that the formation constant of the sydnone–iodine complex is large, it seems likely that the first ionization potential of the sydnone is relatively small, although data on the entropy change with complex formation are unavailable.

Acknowledgment.—We are indebted to Professor M. Ohta of our Institute for the sample of 3-phenylsydnone.

MEGURO-KU, TOKYO, JAPAN

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[16] For the meaning of the sign ± in this formula see W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA

Faradaic Rectification with Control of Alternating Potential Variations—Application to Electrode Kinetics for Fast Processes

BY HIROAKOI MATSUDA[1] AND PAUL DELAHAY

RECEIVED OCTOBER 19, 1959

In this method, the potential of an electrode at which a fast charge transfer process occurs is varied about the equilibrium potential according to a sinusoidal function of time. The resulting alternating current includes a rectification component because of the asymmetry of the current-potential curve. An equation is derived for the faradaic rectification current and is compared with a previous result obtained on the assumption of current control for $t \rightarrow \infty$. A correction for the double layer structure in the solution of the boundary value problem also is derived.

Introduction

A faradaic rectification method for the kinetic study of electrode processes recently was developed by Barker[2,3] from an idea originally advanced by Doss and Agarwal.[4] The method is based on the rectification by an electrode reaction as a result of the asymmetry of its current-potential characteristic with respect to the equilibrium potential (except, of course, for the rare case of symmetry). Thus, a sinusoidal current causes the electrode potential to vary periodically about a mean potential which is different from the equilibrium potential without current. This shift in potential allows the kinetics of the electrode reaction to be studied. Doss and Agarwal[4] gave a theoretical analysis of the method for the particular case of reactants having equal concentrations and equal diffusion coefficients. Barker[3] and, independently, Vdovin[5] generalized this treatment. The former author also considered[3] processes with adsorption, slow electrode reactions, etc. These authors derived the shift of the mean potential on the assumption that there is control of the alternating current whereas in many instances the low impedance of the double layer capacity at the high frequencies (perhaps 1 megacycle per sec.) at which measurements are made results

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[1] Research Associate, 1958–1959; on leave from the Government Chemical Industrial Research Institute, Tokyo.

[2] G. C. Barker, *Anal. Chim. Acta*, **18**, 118 (1958).

[3] G. C. Barker, "Transactions of the Symposium on Electrode Processes, Philadelphia, 1959," E. Yeager ed., John Wiley and Sons, Inc., New York, N. Y., in course of publication.

[4] K. S. G. Doss and H. P. Agarwal, *Proc. Indian Acad. Sci.*, **39**, 263 (1951); **35A**, 45 (1952).

[5] Iu. A. Vdovin, *Doklady Akad. Nauk SSSR*, **120**, 554 (1958).