Kinetics of Transformation of Outer Charge-Transfer Complexes to Inner Complexes[1a]

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Abstract: Kinetics of transformation of outer charge-transfer complexes to inner complexes are found to follow the first-order rate law. The rate constants and energies of activation are markedly affected by solvent dielectric constant as well as electrical effects of substituents on the donors. The ease with which the transformation proceeds depends on the relative magnitudes of the enthalpy of formation of the outer complex and the energy of activation of the transformation. The electrostatic contribution to the observed large negative entropies of activation is found to be small.

Mulliken[2] pointed out that a donor–acceptor pair can form either the associative outer complex or the dissociative inner complex depending on the distance of approach between the donor and acceptor and the relative magnitude of the no-bond and dative wave functions. It was also suggested that the formation of the inner complex from the outer complex should be strongly dependent on environmental conditions. One of the early evidences for the transformation of outer complexes to the inner variety was the electrical conductance of iodine in pyridine which was explained[3] on the basis of the equilibrium

$$\underset{\text{outer complex}}{C_5H_5N\cdot I_2} \rightleftharpoons \underset{\text{inner complex}}{C_5H_5N^+I + I^-}$$

Examination of the literature shows that in many donor–acceptor systems with halogen acceptors, the formation of trihalide ion is often noticed which can only result through the formation of inner complexes from the initial outer complexes. In view of the limited information available in the literature, we have now investigated the transformation of a few outer complexes between n donors with iodine, with particular reference to the factors affecting the formation of inner complexes. Some kinetic aspects of this ionization reaction have also been examined.

Results and Discussion

Triphenylarsine and triphenylstibine form 1:1 outer charge-transfer complexes with iodine[4] with λ^{CT}_{max} at 320 and 290 mμ, respectively. The equilibrium constants of formation are 8300 and 1700 l. mole^{-1}, respectively, at 25°, while the enthalpy values are 1.6 and 3.0 kcal mole^{-1}. The intensity of the charge-transfer bands in these two systems decreases markedly with time. Accompanying the decrease in the intensity of the charge-transfer bands, progressive intensification of the triiodide ion absorption at 297 and 363 mμ is noticed. It was felt that the time dependence of the charge-transfer bands and the formation of I_3^- were both due to the transformation of the initially formed 1:1 outer complex into the inner complex followed by the fast reaction of the inner complex with iodine to form the triiodide ion.

$$\underset{M\,=\,\text{As or Sb}}{(C_6H_5)_3M + I_2} \rightleftharpoons \underset{\text{outer complex}}{(C_6H_5)_3M\cdot I_2} \xrightarrow{\text{slow}} \underset{\text{inner complex}}{(C_6H_5)_3M^+I\ I^-}$$

$$(C_6H_5)_3M^+I\ I^- + I_2 \rightleftharpoons (C_6H_5)_3M^+I\ I_3^-$$

The quaternary salts (inner complexes) have already been reported in both the arsine and stibine systems.[4]

The kinetics of the transformation of the outer complexes, $(C_6H_5)_3As\cdot I_2$ and $(C_6H_5)_3Sb\cdot I_2$, to the corresponding inner complexes are of first order and the rate constants are quite large. The rate data are summarized in Table I along with the values of the energies and entropies of activation. It can be seen that there is an appreciable decrease in the energy of activation with the increase in the dielectric constant of the medium. In a polar solvent like methylene chloride, the transformation is very fast and the triiodide ion appears almost immediately after mixing $(C_6H_5)_3As$ with iodine.

The transformation of the outer complex, $(C_6H_5)_3Sb\cdot I_2$, to the inner complex is much slower and is associated with a higher activation energy (E_a) than the transformation of $(C_6H_5)_3As\cdot I_2$. It is interesting that the enthalpy value for the formation of the outer complex ($-\Delta H$) is also much lower in the latter case. Apparently, a stable outer complex (associated with greater charge transfer in the ground state as well as a higher value of $-\Delta H$) shows a larger E_a for the transformation than a weaker outer complex. The magnitude of E_a directly determines the facility with which the transformation of the outer complex to the inner complex occurs, since the formation of the outer complex itself is not a rate-determining step. In the case of $(C_6H_5)_3Sb\cdot I_2$, where the $-\Delta H$ value is large, E_a is also large and the transformation proceeds appreciably slower than in $(C_6H_5)_3As\cdot I_2$. Triphenylphosphine, on the other hand, is known to form halophosphine halides[4,5] immediately after the addition of halogens to $(C_6H_5)_3P$, which indicates a very low value of E_a for the transformation (and possibly a low $-\Delta H$ value for the outer complex as well).

There is abundance of data in the literature which suggests that trihalide ion is formed by the reaction of a halogen with n donors. Typical of such systems are di-

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[1] (a) Taken in part from the Ph.D. thesis to be submitted by S. N. B. to the Indian Institute of Technology, Kanpur; (b) to whom all the correspondence should be addressed.

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Table I. Rate Data on the Transformation of the Outer Complexes of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ with Iodine

		$(C_6H_5)_3As + I_2$[a]			$(C_6H_5)_3Sb + I_2$[a]		
Solvent	D	k,[b] min^{-1} ($\times 10^3$)	E_a, kcal $mole^{-1}$	ΔS^*, eu	k,[b] min^{-1} ($\times 10^3$)	E_a, kcal $mole^{-1}$	ΔS^*, eu
CCl_4	2.2	5.6	4	−64	1.3	6	−65
$CHCl_3$	4.5	15.0	3	−70	1.9	3	−73
CH_2Cl_2	9.1	41.0	1	−77	2.6	2	−77

[a] Donor concentration 2.56×10^{-4} M; I_2 concentration 4×10^{-5} M. [b] Temperature 26°.

Table II. Rate Data on the Transformation of the Outer Complexes of DMSO and Acetone with Iodine

Donor concn.[a] (DMSO)	D	k, min^{-1} ($\times 10^3$)[b]	E_a, kcal $mole^{-1}$	ΔS^*, eu	Donor concn[a] (acetone)	D	k, min^{-1} ($\times 10^3$)	E_a, kcal $mole^{-1}$	ΔS^*, eu
0.30	2.5	0.67	...	...	...	...	...	...	...
0.51	3.3	1.20	9.5	−51	1.70	3.3	1.0	9.3	−52
1.00[c]	4.3	2.10	9.0	−53	3.30	4.3	4.9	...	...
3.00	8.9	8.30	8.5	−49	7.30[d]	9.0	38.0	...	...
5.10	14.0	14.10	8.0	−52	...	...	...	...	...

[a] In CCl_4 solvent; I_2 concentration 9.8×10^{-5} M. [b] At 26°. [c] With 1.0 M DMSO in $CHCl_3$ ($D = 7.3$), k was 4.9×10^{-3} min^{-1} with E_a of 8.8 kcal $mole^{-1}$ and ΔS^* of −56 eu. [d] With 1.6 M acetone in $CHCl_3$ ($D = 6.5$), k was 6.4×10^{-3} min^{-1} with E_a of 5.0 kcal $mole^{-1}$ and ΔS^* of −60 eu.

methyl sulfoxide + iodine and acetone + iodine.[6] Even though unique charge-transfer bands corresponding to the outer complexes are not observed in such systems, it is probable that the triiodide is formed through the transformation of the outer complexes to the inner complexes. The formation of triiodide ion is a function of time, concentration of the donor, and nature of the solvent. Thus, in the study of the interaction of iodine with aliphatic ketones, it is found that saturated hydrocarbon solvents are much superior to CCl_4 or $CHCl_3$. Further, high ketone concentrations which are necessary for the study of equilibria in such weakly interacting systems favor the formation of the triiodide ion, possibly owing to the relatively high dielectric constants of the media.

Since the formation of the triiodide ion from the inner complex is likely to be a fast step, the rate-determining step in the formation of the triiodide ion is probably the transformation of the outer complex.[7] The results of the kinetic studies on the formation of I_3^- in DMSO–I_2 and $(CH_3)_2CO$–I_2 systems are shown in Table II. It can be seen that the rates are of first order and that the activation energy decreases with increase in the dielectric constant of the medium just as in the transformation of $(C_6H_5)_3M \cdot I_2$ (M = As or Sb), where the kinetics were studied by the decrease in intensity of the charge-transfer band. The enthalpies of formation of the outer complexes for DMSO–I_2 and $(CH_3)_2CO$–I_2 are both about 3.7 kcal $mole^{-1}$.[6,7]

Person and co-workers[8] have recently shown that the interaction of aliphatic nitriles, RCN, with iodine decreases with the electron-withdrawing power of the substituent R. Aliphatic nitriles are also known to give trihalide ions as a function of time on interaction with halogens.[9] It was therefore considered interesting to study the interaction of a few aliphatic nitriles with iodine, both in terms of the stability of the outer complexes and the facility of transformation to inner complexes. The equilibrium constants of formation of 1:1 complexes for the interaction of acetonitrile and trimethylacetonitrile with iodine were 0.5 and 0.8 l. $mole^{-1}$ at 25° with $-\Delta H$ values of 1.6 and 2.6 kcal $mole^{-1}$, respectively. The data on $CH_3CN \cdot I_2$ agree well with those of Person, *et al.*[8] The equilibrium constant for the interaction of trichloroacetonitrile was too small to measure. The kinetics of formation of triiodide ion in the case of these nitriles are given in Table III, where it can be seen that the first-order rate constant varies in the order $(CH_3)_3CCN > H_3CCN > Cl_3CCN$. The energy of activation decreases in the same order. The results clearly show how substituent effects determine not merely the thermodynamics of formation of outer complexes, but also their transformation to inner complexes. The trends of substituent effects observed are in accord with expectations, since an electron-donating group such as the *t*-butyl group should make the nitrile a stronger donor than the electron-withdrawing CCl_3 group.

Table III. Rate Data on the Transformation of the Outer Complexes of Aliphatic Nitriles, RCN, with Iodine[a]

Donor R =	σ^*[b]	k, min^{-1}[c] $\times 10^3$	E_a, kcal $mole^{-1}$	ΔS^*, eu
t-Bu	−0.30	7.1	2.2	−70
CH_3	0.00	1.7	3.7	−71
CCl_3	+2.65	1.1	5.2	−65

[a] Solvent CCl_4; donor concentration 6.7×10^{-2} M; I_2 concentration 1.4×10^{-2} M. [b] Taft $-\sigma^*$ values for the aliphatic series taken from R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956. [c] At 26°.

The results from this study on the effect of solvent dielectric constant and the electrical properties of sub-

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(7) The mechanism proposed here would not change the amount of titratable iodine. Accordingly, in DMSO–I_2 and in acetone–I_2 systems the titratable iodine was found to be constant with time. The authors are thankful to one of the referees for this suggestion.

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stituents on the transformation of outer charge-transfer complexes to inner complexes are in accordance with the expectations of Mulliken.[2] Mulliken described the energy of interaction between the donors and acceptors as a function of the charge-transfer coordinate (with b/a as the parameter, where b and a are coefficients of the dative and no-bond wave functions) and showed that there should be two important minima in the potential energy curve, one for the loose outer complex and another for the inner complex. He also pointed out that in many donor–acceptor systems, the inner complex may be the more stable form, particularly in solvents favoring solvation of the inner complex or its ions. The formation of stable association products such as I_3^- would be a consequence of the formation of the inner complex.

The entropies of activation, ΔS^*, found in this study for the transformation of outer to inner complexes are large and negative. The ΔS^* values do not vary greatly with the solvent dielectric constant, but the trend is in the expected direction.[10] The negative ΔS^* values are indeed what one would expect in reactions involving ionization of neutral molecules.[10] Since the transformation of the outer to the inner complex involves ionization, it is likely that the activated complex is also similar to an ion pair and will therefore be stabilized by solvation to a greater extent than the outer complex (initial state).[10,11] The observed decrease in the activation energy with increase in the solvent dielectric constant suggests that the solvation is greater for the activation complex. By applying the Kirkwood equation[12] to the transition-state theory[10] for the reaction outer complex (0) $\rightleftharpoons$ activation complex ($*$), one finds

$$\ln k = \ln k_0 - \frac{N}{RT}\frac{(D-1)}{(2D+1)}\left[\frac{\mu_0{}^2}{r_0{}^3} - \frac{\mu_*{}^2}{r_*{}^3}\right] \qquad (1)$$

The term k_0 in the equation stands for the rate constant in a condensed medium of unit dielectric constant, μ for the dipole moment of the species, and r for the radius. According to this equation, the logarithm of the rate constant should vary linearly with $(D-1)/(2D+1)$, where D is the dielectric constant.[13] The kinetic data in Tables I and II show fairly good linear relationships of log k with $(D-1)/(2D+1)$, even though different solvents of varying dielectric constant have been employed in some cases. The relationship is particularly good in the dimethyl sulfoxide–iodine system where the dielectric constant of the medium was varied by varying the concentration of dimethyl sulfoxide. Since such good linear relations are rarely found in the literature for the kinetics of ionization of neutral molecules,[10] it was considered worthwhile to investigate these relations in greater detail.

The electrostatic contribution to the entropy of activation can be calculated by the expression[14]

$$\Delta S_{\mathrm{el}}^* = -\left(\frac{\mu_0{}^2}{r_0{}^2} - \frac{\mu_*{}^2}{r_*{}^3}\right)\frac{3D}{(2D+1)^2}\left(\frac{\partial \ln D}{\partial T}\right)_p \qquad (2)$$

The first term f(μ), can be obtained from the linear plots of log k against $(D-1)/(2D+1)$ following eq 1, while the data for the other terms are available in the literature.[10] The ΔS_{el}^* values calculated from the data in Table I for triphenylarsine and -stibine systems are given in Table IV.

Table IV. Electrostatic Contribution to ΔS^*

Solvent	D	$-\Delta S_{\mathrm{el}}^*$, eu $(C_6H_5)_3As\cdot I_2$[a]	$-\Delta S_{\mathrm{el}}^*$, eu $(C_6H_5)_3Sb\cdot I_2$[b]
CCl_4	2.2	1.0	0.4
$CHCl_3$	4.5	2.5	0.9
CH_2Cl_2	9.1	3.4	1.3

[a] f(μ) = −5.6 kcal. [b] f(μ) = −2.1 kcal.

The ΔS_{el}^* value for the dimethyl sulfoxide–iodine (Table II) was constant around −1.8 eu [f(μ) = −9.4 kcal] in the D range of 3–14. The acetone–iodine system (Table II) gave ΔS_{el}^* which varied from −3 to −7 eu [f(μ) = −15.6 kcal] in the D range of 3–9. These values of $-\Delta S_{\mathrm{el}}^*$ are very low compared to the values calculated by Pearson[14] for a hypothetical ionization reaction assuming a f(μ) of −60 kcal. The f(μ) values found in the present study are also very low. These results are not surprising since the activation entropies (Tables I and II) showed little variation with solvent dielectric constant. It is possible that in these systems the energy of the transition state is lowered to roughly the same extent by nonpolar as well as polar solvents. Further, it must be noted that the application of the classical electrostatic model and the bulk dielectric constants only serves as a rough indication of the solvent effects on the kinetics of such ionic reactions.

Experimental Section

All the materials employed in this study with the exception of trimethylacetonitrile and trichloroacetonitrile were available commercially and were purified before use. These two nitriles were prepared by standard procedures starting from the corresponding carboxylic acids.

Spectrophotometric measurements were made with a Beckman DU spectrophotometer fitted with a variable-temperature compartment. The kinetics of transformation of the outer complexes to the inner complexes were studied by employing the charge-transfer bands in the case of triphenylarsine–iodine and triphenylstibine–iodine systems. The optical densities of the absorption bands were measured at different times (at least five or six points) for the first few per cent of the reaction (within 30–40 min) at three temperatures (in the range 5–45°). The uncertainty in temperatures was ±0.5°. The reactions were found to follow the first-order rate law, and the rate constants were evaluated by subjecting the experimental data to least-squares treatment employing an IBM 1620 computer.

In the case of the dimethyl sulfoxide–iodine system, as well as the acetone–iodine system, since no charge-transfer bands are observed,[6] the kinetics of transformation of the outer complexes were followed by the time dependence of I_3^- absorption bands (297 and 363 mμ). The rate found by the study of either of the I_3^- bands was the same. It was interesting that the development of the I_3^- absorption bands also follow the first-order rate law. In the DMSO-I_2 and $(CH_3)_2CO$-I_2 systems, the concentration of titratable iodine was determined immediately after mixing the iodine solution (of known concentration) with the solutions of the donors and again after several hours.

The energies of activation of the transformations were obtained from the Arrhenius plots of log k against $1/T$. The uncertainty in the value of E_a was generally ±1 kcal mole^{-1}. Entropies of ac-

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tivation were calculated by using the Eyring equation from absolute rate theory.[15]

The interaction of aliphatic nitriles, RCN [R = CCl_3, CH_3, $C(CH_3)_3$], with iodine was studied by the method described by Person and co-workers.[8] The equilibrium constants of interactions were determined for acetonitrile and trimethylacetonitrile by the use of the Rose–Drago equation[16] employing an IBM 1620 computer.

The enthalpies of formation (uncertainty of ±1 kcal $mole^{-1}$) of the 1:1 complexes were calculated from the equilibrium constants at different temperatures. The transformation of outer complexes of nitriles to the inner complexes was studied by employing the I_3^- bands. It is interesting that even though the interaction of trichloroacetonitrile with iodine is very weak,[8] the rate of formation of I_3^- is comparable with that of other nitriles.

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On the Jahn–Teller Effect in Vanadium Hexacarbonyl

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Abstract: It is suggested that the odd-electron species $V(CO)_6$ should experience a Jahn–Teller effect. Comparison of the infrared spectra of gaseous $V(CO)_6$ and $Cr(CO)_6$ gives strong evidence for such an effect because the P, Q, and R branches present in the CO stretching band structure of $Cr(CO)_6$ are absent in $V(CO)_6$. The greater complexity of the electronic spectrum of $V(CO)_6$ compared with that of $Cr(CO)_6$ may be additional evidence for this effect. It is suggested that *probably* there is no static distortion of the O_h symmetry in $V(CO)_6$ but a dynamic Jahn–Teller effect in which the molecule still transforms in its initial higher symmetry group in spite of the coupling between nuclear and electronic motions.

After the discovery of $V(CO)_6$ there existed considerable confusion about the structure of this molecule. The initial investigators suggested a dimeric formula,[1] since no effects of paramagnetism were found in the nmr spectrum in the hydrocarbon solvent even at high carbonyl concentrations. The compound was independently discovered by another group[2] and formulated as monomeric, since it was found to be isomorphous with $Cr(CO)_6$. A later attempt to observe the paramagnetic resonance spectrum was unsuccessful and favored the dimeric formula.[3] Finally, however, exact magnetic measurements showed[4] that the species was paramagnetic in both solid and dissolved states. This, together with the molecular weight determination, proved that the monomeric formula is correct. Recently the esr spectrum was obtained, and a *g* factor close to 2 was found. This is the value expected for one free electron.

In all these investigations it has been silently assumed that the structure of monomeric $V(CO)_6$ is octahedral in similarity to the other metal hexacarbonyls. This assumption must be questioned because of the existence of the Jahn–Teller rule. This rule states that a molecular configuration with an electronically degenerate ground state is not stable. For the group VI-B carbonyls, in which the central metal has six d electrons, the ground state is A_{1g} in the field of a strong ligand such as CO. On the other hand, the ground state of vanadium(0), a d^5 case, must be $^2T_{2g}$ in the octahedral configuration. If a tetragonal distortion is assumed, for example, this is split into $^2B_{2g}$ and ^2E_g terms. The three degenerate d_π orbitals d_{xy}, d_{yz}, and d_{zx} are split in this way into d_{xy} and a degenerate set d_{yz} and d_{zx}. For an elongation along the *z* axis, d_{yz} and d_{zx} should have lower energy, and the state $^2B_{2g}$ made up of $(d_{yz}, d_{zy})^4d_{xy}$ should be the ground state.

On the other hand, previous experience[5] suggests a dynamic rather than a static Jahn–Teller effect. Even though there is coupling between the nuclear and electronic motions, the molecule still transforms in its initial higher symmetry group.[6]

Whereas the dynamic Jahn–Teller effect has been observed for the molecules ReF_6, TcF_6, OsF_6, and RuF_6 (see, for example, ref 6), this is the first attempt to observe it in a metal carbonyl.

Experimental Section

A. The Shape of the CO Stretching Band in $V(CO)_6$. The infrared spectrum of vanadium hexacarbonyl in solution has been reported, and the single CO stretching absorption observed at 1980 cm^{-1} has been described as "broad."[1] This is not expected because the CO stretching band is very sharp for all group VI-B metal hexacarbonyls dissolved in inert solvents such as hydrocarbons. In view, however, of the possible Jahn–Teller effect in $V(CO)_6$, it seemed worthwhile to investigate further this band structure in gaseous $V(CO)_6$.

The infrared spectra calibrated against the known peaks of polystyrene were taken with a Perkin-Elmer Model 521 spectrometer. A heated infrared cell used for gases was alternately filled with $V(CO)_6$ and $Cr(CO)_6$, and the spectra were recorded from 4000 to 700 cm^{-1}. Only the CO stretching absorptions could be detected in $V(CO)_6$ and $Cr(CO)_6$. Figure 1 shows the analogous bands of gaseous $V(CO)_6$ and $Cr(CO)_6$ for comparison. The P, Q, and R branches of the rotational structure are easily distinguishable in the CO stretching vibration of $Cr(CO)_6$ even though the separate rotational lines are not resolved. This is exactly what is expected for a

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