

Study of Charge-Transfer Complexes of [60]- and [70]Fullerenes with a Series of Phosphine Oxides

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Equilibria for the formation of molecular electron donor–acceptor (EDA) complexes of a series of phosphine oxides with [60]- and [70]fullerenes have been studied in CCl₄ medium. An absorption band due to a charge transfer (CT) transition is observed in the visible region. The vertical ionization potentials (I_D^v) of the phosphine oxides determined from the CT transition energies using Mulliken's equation correlate well with those calculated by the semiempirical PM3 method. The experimental I_D^v values also yield good estimates of the electron affinities of [60]- and [70]fullerenes. Among the phosphine oxides studied, triphenyl phosphine oxide, trioctyl phosphine oxide, and tri-*n*-butyl phosphine oxide form stable EDA complexes with [60]- and [70]fullerenes while the complexes of bis-2-ethylhexyl phosphonate with [60]- and [70]fullerenes decay slowly into secondary products. The kinetics of these reactions have been studied by UV–vis absorption spectrophotometric methods, and the rate constants of the decay processes and formation constants of the EDA complexes have been determined at four different temperatures from which enthalpies and entropies of formation of the complexes have been estimated.

1. Introduction

Since the discovery of fullerenes, in particular [60]- and [70]-fullerene,^{1,2} a great amount of work^{3–7} has been done on these two novel π systems. The photophysics of [60]- and [70]-fullerenes in solution is quite well understood.^{8–11} In contrast to planar π electron acceptors, fullerenes possess a number of characteristic features, namely, spherical shape, unique electronic structure, high symmetry, and polarizability.¹² These features provide a certain amount of specificity of the donor–acceptor interaction of fullerenes.

Electron donor–acceptor (EDA) complexes of fullerenes exhibit interesting physical properties (e.g., superconductivity and ferromagnetism)^{13,14} and may be of interest as promising photoactive materials.¹⁵ Charge transfer (CT) in [60]fullerene, conducting polymer composites, and other fullerene-based compounds is currently of great interest since these materials can be utilized in xerography, energy phototransducers, and molecular switches.¹⁶ To date, a great number of molecular complexes of [60]- and [70]fullerenes with cyclotrivenylarenes,¹⁷ crown ethers,¹⁸ calix[*n*]arenes,^{19–24} porphyrines,²⁵ porphyrins,²⁶ etc. have been studied. Konarev et al.²⁷ have determined and utilized the CT transition energies of the complexes of [60]- and [70]fullerenes with a series of tetrathiafulvalenes and related donors to estimate the electron affinities of [60]- and [70]fullerenes. Very recently EDA interaction of fullerenes has been studied with methylbenzenes,^{28,29} polynuclear aromatic hydrocarbons,³⁰ pyridines,³¹ and anilines.³² In all these cases, the CT transition energies have been determined

by electronic absorption spectroscopy and their dependence on vertical ionization potentials (I_D^v) of the donors has been observed.

Syntheses, crystal structures, and some properties of the [60]-fullerene complexes with inorganic elements, namely, (S₈)₂[60]-fullerene, I₂[60]fullerene·C₆H₅CH₃, and (P₄)₂[60]fullerene have been reported.^{33–35} However there is no such report on EDA complex formation of [60]- and [70]fullerenes with *n* donors containing a phosphorus atom. Fullerene complexes with phosphine oxides are of current interest due to the potential ability of the phosphine oxides to bind metal ions, a property which is utilized in a synergistic extraction process.^{36,37} So, it is felt necessary to see whether phosphine oxides bind fullerenes through the formation of EDA complexes. In the present study, we examine the EDA interaction of [60]- and [70]fullerenes with a series of phosphine oxides, viz., tri-*n*-octyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPPO), tri-*n*-butyl phosphine oxide (TBPO), and bis-2-ethylhexyl phosphonate (BEHP) by electronic absorption spectroscopic study in CCl₄ medium. For TPPO, TOPO, and TBP, the EDA complexes are found to be stable with 1:1 (donor–acceptor) stoichiometry, while the other phosphine oxide, i.e., BEHP, forms labile complexes with [60]- and [70]fullerenes. The CT absorption bands are located in each case, and some important parameters have been determined from the trends in such bands. The new feature of the present study is that the kinetics of the decay processes of the two labile complexes has been investigated. To our knowledge, this is the first report on any chemical reaction of a fullerene in its ground state, although reports on ultrafast rate studies with fullerenes in excited states are plenty.^{38–43}

2. Experimental Section

[60]Fullerene was collected from Sigma and [70]fullerene from SES Research Corporation, Houston. The phosphine oxides

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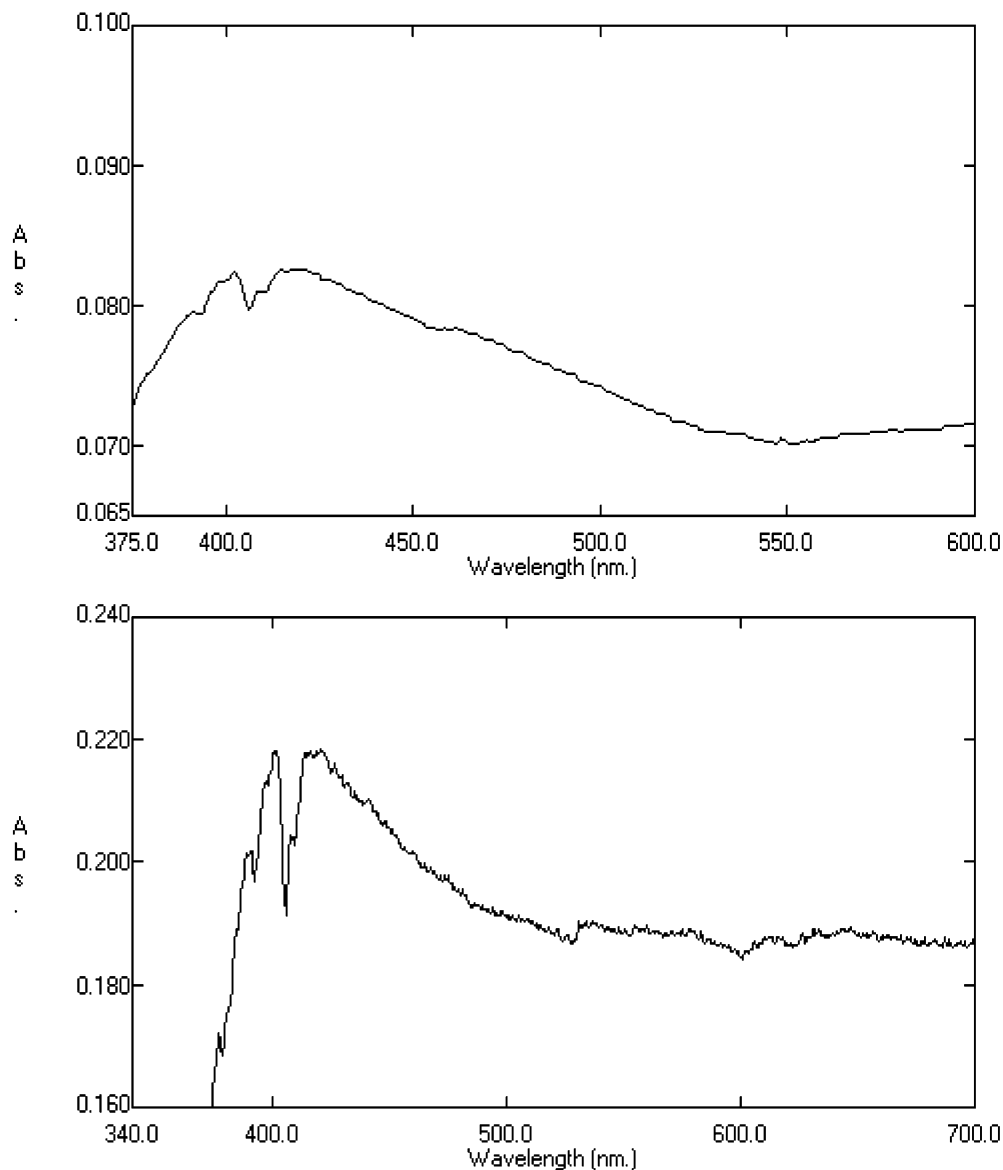


Figure 1. CT absorption spectra of (a) [60]fullerene ($3.4720 \times 10^{-5} \text{ mol dm}^{-3}$) + TOPO ($4.06 \times 10^{-2} \text{ mol dm}^{-3}$) and (b) [70]fullerene ($1.7857 \times 10^{-5} \text{ mol dm}^{-3}$) + TPPO ($0.127 \text{ mol dm}^{-3}$) against pristine acceptor solution as reference.

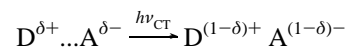
were collected from Lancaster, U.K. The solvent, CCl_4 , was purified by drying over fused CaCl_2 followed by distillation just before use. Spectral measurements were done on a Shimadzu UV-1601 PC model spectrophotometer fitted with a Peltier-controlled thermo bath.

3. Results and Discussions

3.1. Observation of CT Bands. To obtain the CT bands, spectra of each solution (in CCl_4) containing the phosphine oxide–fullerene mixture were recorded against the pristine fullerene solution as reference. It is a common experience that in order to detect the CT bands in solution, the donor concentration must be made very high compared to that of the acceptor. In the present case, [fullerene] $\approx 10^{-5} \text{ mol dm}^{-3}$ and [phosphine oxide] $\approx 10^{-2} \text{ mol dm}^{-3}$ in the mixture. The solvent CCl_4 and the phosphine oxides do not absorb in the visible region. It is important to mention that the complexes of BEHP with [60]- and [70]fullerenes decay into secondary products. So, for these two complexes, CT bands were located by minimizing the reaction rate; the component solutions were cooled first to 278 K and mixed, and spectra were recorded as

quickly as possible. Two representative CT absorption spectra are shown in Figure 1. The energies ($h\nu_{\text{CT}}$) corresponding to the maxima of the CT bands for the various EDA complexes are given in Table 1.

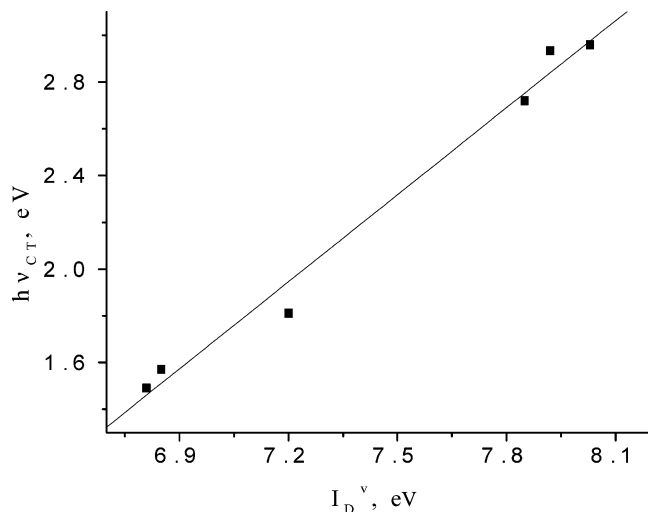
3.2. Determination of Vertical Ionization Potentials (I_{D}^{v}) of Phosphine Oxides. For complexes with a neutral ground state, a CT band corresponds to a transfer of an electron from a donor to an acceptor molecule with absorption of a quantum



The relationship between the energy ($h\nu_{\text{CT}}$) of the lowest-energy intermolecular CT band and I_{D}^{v} of the donor for a series of complexes with a common acceptor has been the source of much discussion. To get the ionization potentials of the phosphine oxide donors, the following procedure was adopted. The experimental CT transition energies ($h\nu_{\text{CT}}$) of complexes of [60]-fullerene with some known donors such as methylbenzenes²⁹ and calix[n]arenes⁴⁴ were plotted against the ionization potentials of the donors (Figure 2). The following linear correlation was

TABLE 1: CT Absorption Maxima and Transition Energies of [60]- and [70]Fullerenes with Phosphine Oxide Complexes, Experimental, Ab Initio, and PM3-Determined Ionization Potential of the Donors, and Degrees of Charge Transfer (α) of the Complexes

donor	λ_{CT} , nm		$h\nu_{CT}$, eV		expt I_D^v (eV)	PM3 I_D (eV)	ab initio I_D (eV)	degree of charge transfer (α)	
	[60]fullerene	[70]fullerene	[60]fullerene	[70]fullerene				[60]fullerene	[70]fullerene
TPPO	413	387	3.00	3.20	8.125	9.781	9.276	0.021	0.0223
TOPO	420	514	2.95	2.41	7.680	9.740	10.253	0.023	0.024
TBPO	420	530	2.95	2.34	7.680	9.723	10.321	0.023	0.024
BEHP	417	409	3.07	3.03	7.310	9.404	10.279	0.024	0.026

**Figure 2.** Plot of $h\nu_{CT}$ vs I_D^v of the donors.

found with a correlation coefficient of 0.99.

$$h\nu_{CT} = (1.34 \pm 0.07)I_D^v - (7.00 \pm 0.54) \quad (1)$$

Now by fitting the presently determined $h\nu_{CT}$ values of the phosphine oxide–fullerene complexes in the above graph, we have obtained the I_D^v values of the phosphine oxides. Results are given in Table 1. These experimental I_D^v values of the phosphine oxides were compared with the theoretical values calculated by the semiempirical PM3 method and also by the ab initio method using the 3-21G* basis set. While the trend in PM3 values is the same as that in the experimental values, the ab initio results show a bit of a scatter. However, the experimental observation that TOPO and TBPO have the same I_D^v is corroborated by both the theoretical methods. It is further noted that the experimental I_D^v values are lower than the theoretical ones; this may be attributed to the fact that theoretical calculations on an isolated molecule do not consider bulk effects, particularly, solvation.

3.3. Determination of Vertical Electron Affinity (E_A^v) of [60] and [70]Fullerenes. The energy of a CT transition can be expressed according to Mulliken's theory⁴⁵ as

$$h\nu_{CT} = I_D^v - C_1 + C_2/(I_D^v - C_1) \quad (2)$$

where C_1 is composed of the electron affinity of the acceptor, electrostatic interactions, and other terms. C_2 is related to the overlap of donating and accepting orbitals, and for a given acceptor, it may be assumed to be constant. Now the quantity C_1 of eq 1 is given by

$$C_1 = E_A^v + G_0 + G_1 \quad (3)$$

where E_A^v is the vertical electron affinity of the acceptor, G_0 is the sum of several energy terms (i.e., dipole–dipole, van der Waals interaction, etc.) in the “no-bond” state, and G_1 is the

sum of the energy terms in the dative state. In most cases, G_0 is small and can be neglected whereas G_1 is largely the electrostatic energy of attraction between D^+ and A^- . A rearrangement of eq 1 yields

$$2I_D^v - h\nu_{CT} = (1/C_1)I_D^v(I_D^v - h\nu_{CT}) + C_1 + C_2/C_1 \quad (4)$$

By use of the observed transition energies and the experimentally determined ionization potentials (shown in Table 1), we have obtained the following correlations: [60]fullerene–phosphine oxide

$$2I_D^v - h\nu_{CT} = (0.1613 \pm 0.00351)I_D^v(I_D^v - h\nu_{CT}) + (6.5312 \pm 0.1291) \quad (5)$$

[70]fullerene–phosphine oxide

$$2I_D^v - h\nu_{CT} = (0.1524 \pm 0.0127)I_D^v(I_D^v - h\nu_{CT}) + (6.8313 \pm 0.4887) \quad (6)$$

with a correlation coefficient of 0.99 in each case. This confirms the CT nature of the observed transitions. A comparison of eqs 4 with 5 and 6 yields $C_1 = 6.20$ and 6.56 eV for [60]- and [70]fullerene, respectively. Neglecting G_0 and taking the typical D–A distance in EDA complexes to be 3.5 \AA , the major part of G_1 is estimated to be $e^2/4\pi\epsilon_0 r = 4.13$ eV. Now by use of eq 3, E_A^v values of [60]- and [70]fullerene in solution are found to be (2.07 ± 0.4) and (2.43 ± 0.2) eV, respectively, which are somewhat less than 2.65 and 2.73 eV, respectively, obtained in the gas phase by Boltalina et al.⁴⁶ and Chen et al.⁴⁷ The difference between the electron affinity values in the gas phase and in solution is due to solvation effect, which makes a significant contribution to G_1 . Because of lack of suitable data, this contribution cannot be estimated correctly.

3.4. Degrees of Charge Transfer (α). In a Mulliken two-state model,³⁹ the ground-state (ψ_g) and excited-state (ψ_{ex}) wave functions of the CT complexes are described by a linear combination of dative $\psi(D^0, A^0)$ and ionic $\psi(D^+, A^-)$ states

$$\psi_g = \{\sqrt{1 - \alpha}\} \psi(D^0, A^0) + \{\sqrt{\alpha}\} \psi(D^+, A^-) \quad (7)$$

$$\psi_{ex} = \{\sqrt{1 - \alpha}\} \psi(D^+, A^-) - \{\sqrt{\alpha}\} \psi(D^0, A^0) \quad (8)$$

where α is the degree of charge transfer. The function $\psi(D^+, A^-)$ differs from $\psi(D^0, A^0)$ by the promotion of an electron from the donor to the acceptor. α is given by^{45,48}

$$\alpha = (C_2/2)/[(I_D^v - E_A^v + C_1)^2 + C_2/2] \quad (9)$$

The values of α (calculated by using eq 9 and given in Table 1) are small and indicate that very little charge transfer occurs in the ground state (about 2%). It is also observed that α decreases with the increasing ionization potentials of the donors, as expected.

3.5. Determination of Formation Constant (K) of the Kinetically Stable Complexes. Because of low intensities of the CT peaks, variation of their intensity with change in donor

TABLE 2: Data for Spectrophotometric Determination of Stoichiometry, Formation Constants (K), and Corrected Molar Absorptivities (ϵ') of the [60]Fullerene–TOPO Complex

temp, K	10^2 donor concentration (mol dm $^{-3}$)	$10^5 [A]_0$ (mol dm $^{-3}$)	absorbances at 600 nm	K (dm 3 mol $^{-1}$)	$10^{-3}\epsilon'$ (dm 3 mol $^{-1}$ cm $^{-1}$)
289	2.62		0.036	38.0 ± 0.4	
	2.74		0.138		
	3.35		0.150		
	3.50		0.159		
	4.06		0.167		
298	2.62		0.133	26.0 ± 0.6	
	2.74		0.136		
	3.35		0.151		
	3.50		0.159		
	4.06	3.472	0.160		8.3 ± 0.7
305	2.62		0.125	14.7 ± 1.4	
	2.74		0.129		
	3.35		0.138		
	3.50		0.150		
	4.06		0.159		
311	2.62		0.117	12.0 ± 1.2	
	2.74		0.122		
	3.35		0.129		
	3.50		0.138		
	4.06		0.150		

concentration could not be employed for determination of stoichiometry and formation constants (K) of the complexes. Instead, it was observed that the intensity of the broad absorption bands of [60]- and [70]fullerenes (measured against the solvent as reference), which are centered more or less at 600 and 472 nm, respectively, increased systematically with gradual addition of the donors, and this fact was utilized to determine K by using the Benesi–Hildebrand⁴⁹ equation for cells with 1 cm optical length

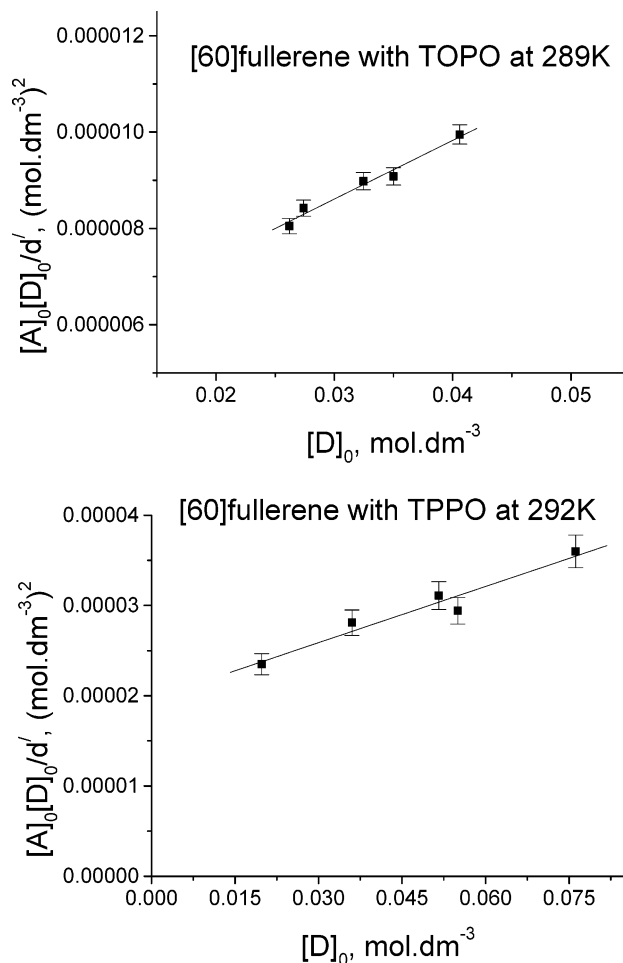
$$[A]_0 [D]_0 / d' = [D]_0 / \epsilon' + 1/K\epsilon' \quad (10)$$

with

$$d' = d - d_A^0 - d_D^0 \quad (11)$$

Here $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor, respectively, d is the absorbance of the donor–acceptor mixture measured against the solvent as reference, and d_A^0 and d_D^0 are the absorbances of the acceptor and donor solutions with the same molar concentrations as in the mixture. All absorbances were measured at 600 nm for [60]fullerene complexes and at 472 nm for the [70]fullerene complexes. The quantity $\epsilon' = \epsilon_c - \epsilon_A - \epsilon_D$ is the corrected molar absorptivity of the complex; ϵ_A and ϵ_D are those of the acceptor and the donor, respectively. K is the formation constant of the complex. Equation 10 is valid⁴⁹ under the condition $[D]_0 \gg [A]_0$ for a 1:1 donor–acceptor complex. Absorbance data for one typical case is shown Table 2. In all the cases, very good linear plots according to eq 10 were obtained; two such cases are shown in Figure 3. Values of K at four different temperatures obtained from such plots are shown in Table 3. It is observed that with the same donor in a given solvent, the formation constant of the [70]fullerene complex is higher than that of the corresponding [60]fullerene complex. This is in conformity with that obtained in some of our earlier works.^{28–30}

3.6. Enthalpies (ΔH_f^0) and Entropies of Formation (ΔS_f^0) of the Kinetically Stable Complexes. The enthalpies (ΔH_f^0) and entropies of formation (ΔS_f^0) of the complexes have been determined by using eq 12, which is the integrated form of the

**Figure 3.** Benesi–Hildebrand plots for the complexes of [60]fullerene with TOPO and TPPO.

well-known van't Hoff equation. As measured, these terms will represent the net change in enthalpy and entropy for the solvated species.

$$\ln K = -\Delta H_f^0/RT + \text{constant} \quad (12)$$

Values of K at four different temperatures are summarized in Table 3. The following linear regression equations have been obtained with the present data: TOPO–[60]fullerene complex

$$\ln K = 4908/T - 13 \quad \text{correlation coefficient} = 0.99 \quad (13a)$$

TPPO–[60]fullerene complex

$$\ln K = 4411/T - 12 \quad \text{correlation coefficient} = 0.98 \quad (13b)$$

TBPO–[60]fullerene complex

$$\ln K = 3652/T - 5 \quad \text{correlation coefficient} = 0.97 \quad (13c)$$

TOPO–[70]fullerene complex

$$\ln K = 6473/T - 17 \quad \text{correlation coefficient} = 0.98 \quad (13d)$$

TPPO–[70]fullerene complex

$$\ln K = 2300/T - 4 \quad \text{correlation coefficient} = 0.97 \quad (13e)$$

TBPO–[70]fullerene complex

$$\ln K = 5584/T - 12 \quad \text{correlation coefficient} = 0.99 \quad (13f)$$

The positive slope in each case indicates that the complexation process is exothermic and thus driven by favorable enthalpy

TABLE 3: Enthalpies and Entropies of Formation for the Complexes of Phosphine Oxides with [60]- and [70]Fullerenes

donor	formation constant/dm ³ mol ⁻¹ (temp/K)		ΔH_f^0 , kJ mol ⁻¹		ΔS_f^0 , JK ⁻¹ mol ⁻¹	
	[60]fullerene	[70]fullerene	[60]fullerene	[70]fullerene	[60]fullerene	[70]fullerene
TPPO	10.5 ± 0.7 (292)	24.0 ± 5.2 (291)	-36.7 ± 5.7	-19.1 ± 3.2	-107.0 ± 19.0	-39.2 ± 11.1
	9.1 ± 2.6 (299)	20.0 ± 3.1 (300)				
	5.8 ± 0.9 (306)	16.5 ± 0.5 (305)				
	3.9 ± 1.7 (313)	15.0 ± 0.5 (311)				
TOPO	38.0 ± 0.4 (289)	67.0 ± 1.8 (293)	-40.8 ± 4.5	-53.8 ± 4.5	-110.9 ± 15.6	-148.6 ± 28.7
	26.0 ± 0.6 (298)	57.0 ± 6.9 (298)				
	14.7 ± 1.4 (305)	31.0 ± 1.8 (303)				
	12.0 ± 1.2 (311)	23.0 ± 0.3 (309)				
TBPO	865 ± 45 (293)	1510 ± 72 (293)	-32.64 ± 3.25	-55.64 ± 11.2	-35.23 ± 1.67	-59.38 ± 5.70
	615 ± 50 (299)	1100 ± 40 (299)				
	530 ± 45 (305)	820 ± 60 (305)				
	385 ± 25 (311)	660 ± 65 (311)				

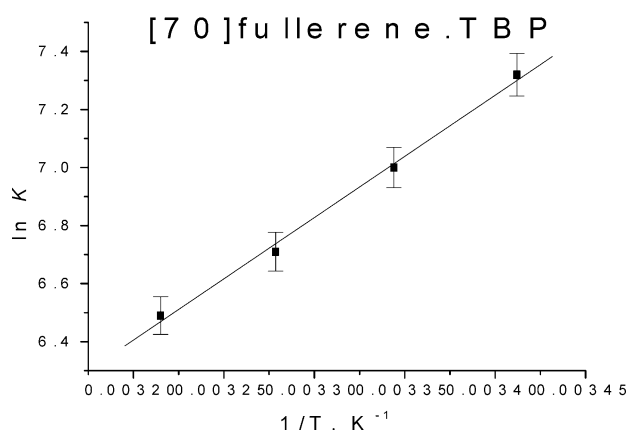
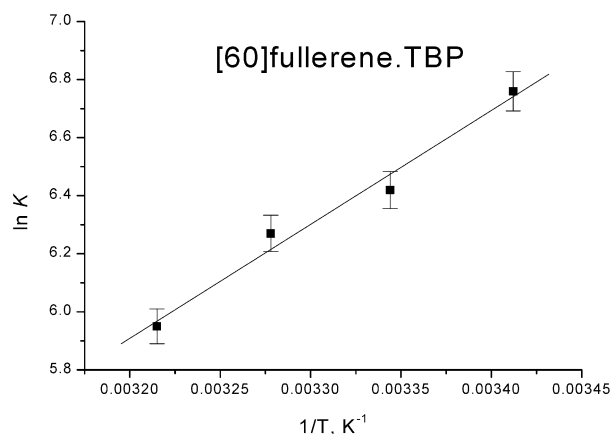
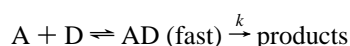


Figure 4. Plot for determination of enthalpy of formation of the complexes of TBP with [60]- and [70]fullerenes.

changes. The ΔH_f^0 and ΔS_f^0 values of the complexes are shown in Table 3. Two typical plots of $\ln K$ against $1/T$ are shown in Figure 4.

3.7. Results of Kinetic Studies. A complex of bis-2-ethylhexyl phosphonate (D) with [60]fullerene (A) was formed instantaneously upon mixing the solutions of D and A in CCl_4 medium, and intensity of the CT band increased with time from the very beginning (Figure 5). This was indicative of product formation, the product absorption band overlapping with the CT band ($\lambda_{\text{CT}} = 417 \text{ nm}$) of the intermediate EDA complex. Variation of absorbance of the D-A mixture with time at this wavelength conforms to the following reaction scheme



in terms of the concentration of the product, the rate equation

is given by

$$d[P]/dt = k[AD] \approx kK[A]_0[D]_0 \quad (14)$$

which on integration yields

$$[P] = kK[A]_0[D]_0 t + Z_1 \quad (15)$$

When $t = 0$, no product is formed. Thus

$$Z_1 = 0 \quad (16)$$

$$[P] = kK[A]_0[D]_0 t$$

Now the absorbance (d) at 417 nm, where the product and, presumably, also the complex absorbs, is given by

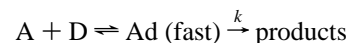
$$d = \epsilon_P[P]l + \epsilon_{AD}K[A]_0[D]_0 l \quad (17)$$

where ϵ_P and ϵ_{AD} represent the molar extinction coefficients of the product and the complex AD, respectively, and l is the optical length. When $l = 1 \text{ cm}$, rearrangement of eq 17 gives

$$d = kK[A]_0[D]_0 t \epsilon_P + \epsilon_{AD}K[A]_0[D]_0 \quad (18)$$

Experimentally observed absorbance values at 417 nm at different instants of time for the BEHP-[60]fullerene mixture fit eq 18 excellently with a correlation coefficient of 0.99. This supports the proposed reaction scheme. An effective rate constant, viz., $k\epsilon_P/\epsilon_{AD}$, can be obtained from the slope/intercept of such a plot. The calculated value is $(8 \pm 1) \times 10^{-3}$.

The complex of BEHP with [70]fullerene also started to decay from the very beginning (Figure 6). This was indicated by the decrease in intensity at the $\lambda_{\text{CT}} (=409)$ with time. In this case, the product absorption band evidently does not overlap with the CT absorption band of the intermediate EDA complex. The same reaction scheme as before was tried



Here A is [70]fullerene. The rate equation is

$$-d[\text{complex}]/dt = k[\text{complex}] \quad (19)$$

which on integration yields

$$[\text{complex}] = [\text{complex}]_0 \exp(-kt) \quad (20)$$

where the square bracket denotes concentration and the subscript zero corresponds to $t = 0$.

If BEHP (D) is taken in large excess, the concentration of

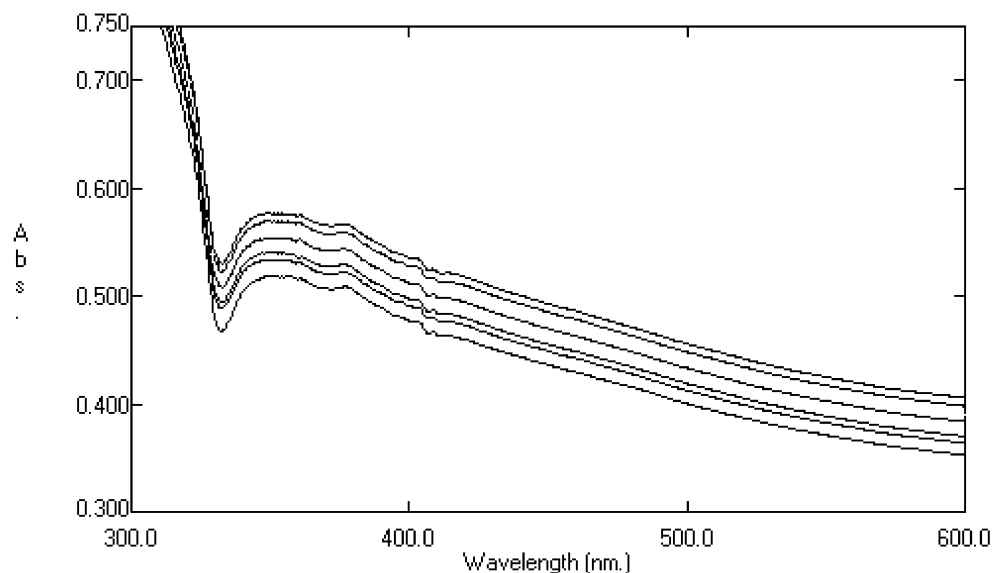


Figure 5. Variation of absorption spectrum of the [60]fullerene-BEHP mixture with time. $[(60)\text{fullerene}] = 6.569 \times 10^{-6} \text{ mol dm}^{-3}$. $[\text{BEHP}] = 1.875 \text{ mol dm}^{-3}$.

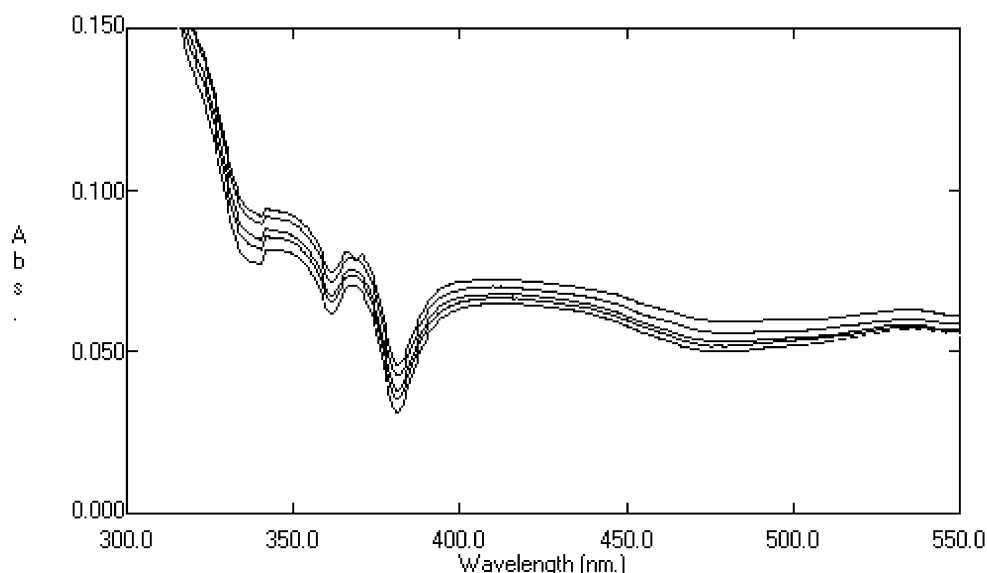


Figure 6. Variation of absorption spectrum of the [70]fullerene-BEHP mixture with time. $[(70)\text{fullerene}] = 9.39 \times 10^{-6} \text{ mol dm}^{-3}$. $[\text{BEHP}] = 2.143 \text{ mol dm}^{-3}$.

[70]fullerene (A) at any time t is given by

$$[A] = [AD]/K[D] \approx [AD]/K[D]_0 = [AD]_0 \exp(-kt)/K[D]_0 \quad (21)$$

which simplifies to

$$\ln[A] = \ln[AD]_0 - kt - \ln[K] + \ln[D]_0 \quad (22)$$

or

$$\ln d = -kt + Z_2 \quad (23)$$

where Z_2 is a constant and d is the absorbance of the mixture at time t . The rate constant obtained from the slope of the $\ln d$ vs t plot is $(4.2 \pm 0.1) \times 10^{-3} \text{ min}^{-1}$ (Figure 7).

4. Conclusions

The present study demonstrates significant ground-state complex formation between [60]- and [70]fullerenes with

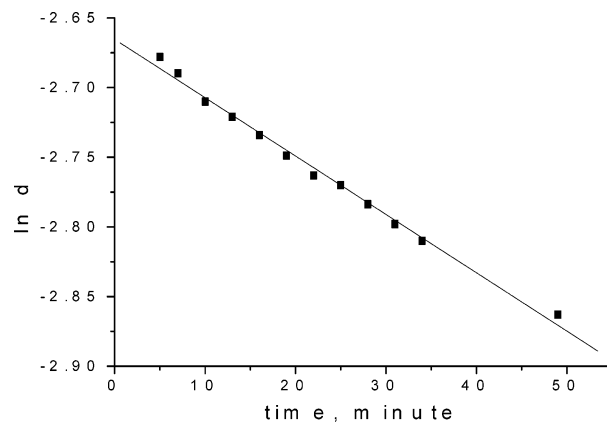


Figure 7. Plot of $\ln d$ vs time for the [70]fullerene-BEHP complex.

phosphine oxides. The $h\nu_{CT}-I_D^V$ dependence has been exploited to determine the vertical ionization potentials of the phosphine oxides. The experimental I_D^V values are somewhat less than those obtained by semiempirical PM3 calculations, although the

trends are in the same direction. This difference may be attributed to solvation effect; PM3 calculation considers an isolated phosphine oxide molecule in the gas phase while the present experimental values are based on solution data. Reasonable values of vertical electron affinity of [60]- and [70]-fullerenes in solution have been obtained. The very low values of α indicate that the CT complexes studied here have almost neutral character in their ground states. An important aspect of the present study is that it reports for the first time kinetic study of a slow chemical reaction of the two fullerenes in their ground state with one phosphine oxide, viz., BEHP; the labile BEHP–fullerene complexes decay by a path first order with respect to the complexes.

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References and Notes

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