In the following we shall assume that the observed rate constant $k = k_e$, i.e., that proton transfer is diffusion controlled, and that the steric factor for reaction is unity, and by means of (14) or (15) calculate σ for each reaction. Although these σ values may not represent real encounter diameters, they do represent an index of reactivity that has been corrected for differences in mobility and charge type of the reactants.

The results of the calculation are listed in Table III. The σ values divide themselves roughly into two groups. For all reactions with OH^-, and (surprisingly) for the reaction of I with $P_2O_7^{4-}$, σ is in the range 2.8 ± 0.5 Å, which is of an acceptable magnitude for a real encounter diameter. (Compare with the nearest neighbor O–O distance of 2.76 Å in ice.) The other values are too small, by significant amounts, to represent genuine closest approach distances. Here, if we wish to retain the model of diffusion-controlled reaction with steric factors of unity, we must infer that (14) and (15) overestimate the true value of k_e. A likely reason for this is that in the stepwise diffusion process preceding the formation of the reactive encounter complex, the final step or steps have higher activation free energies than that for diffusion of the far-separated A and B molecules in the bulk solvent. In other words, the formation of the encounter complex is opposed by forces of solvation, since it involves the mutual penetration and distortion of the original solvation shells of the A and B molecules.

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An X-Ray Structure Determination of the 1:1 Charge Transfer Complex of Naphthalene and Tetrachlorophthalic Anhydride at −153°

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Abstract: The crystal structure of the 1:1 charge transfer complex of perdeuterated naphthalene and tetrachlorophthalic anhydride has been determined at −153°. Crystals of the complex grow in the form of light-yellow triclinic needles ($P\bar{1}$; $Z = 2$), with unit cell dimensions $a = 10.042$ (5), $b = 6.701$ (2), $c = 13.872$ (9) Å, $\alpha = 86.34$ (4), $\beta = 90.82$ (5), and $\gamma = 59.63$ (3)°. The structure was solved with Patterson and Fourier techniques and refined by least squares to a conventional R value of 0.048 for 2044 observed reflections collected on a Syntex $P\bar{1}$ autodiffractometer with Mo Kα radiation. Component molecules are stacked alternately in infinite chains along the b axis. Accurate, low temperature, structural parameters obtained for naphthalene and tetrachlorophthalic anhydride in the complex are within experimental error identical to those observed in the pure materials.

Accuracy of X-ray structural determinations for charge transfer complexes of the π–π type has often been limited by the large thermal motion and disorder exhibited by one of the molecular components. Complexes of naphthalene seem to be particularly susceptible to this problem.[1] In both the naphthalene–tetracyanobenzene[2] and naphthalene–tetracyanoethylene[3] complexes the naphthalene molecules are disordered at room temperature. Although detailed structural data are not available, the naphthalene–trinitrobenzene and naphthalene–pyromellitic dianhydride complexes also appear to be disordered.[1]

Because of the theoretical interest in the detailed molecular parameters of naphthalene, a very careful determination of the crystal structure of pure naphthalene has been carried out[4] in which corrections for the thermal motion were applied. An electron diffraction study of gaseous naphthalene has also been reported.[5] Although very few data of comparable accuracy appear to be available for molecular π complexes of naphthalene, structures of two inorganic naphthalene complexes have been determined. In the unusual naphthalene–$AgClO_4$ complex[6] the naphthalene molecule is ordered, but the accuracy of C–C bond lengths ob-

Table I. Final Atomic Parameters[a,b]

	Positional parameters for TCPA			Anisotropic temperature factors for TCPA					
	x	y	z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Cl(1)	0.2403 (1)	0.0354 (2)	0.0238 (1)	60 (1)	176 (4)	15 (1)	−41 (2)	5 (1)	−5 (1)
Cl(2)	0.5634 (1)	−0.2181 (2)	0.1351 (1)	33 (1)	114 (4)	27 (1)	−30 (2)	10 (1)	−14 (1)
Cl(3)	0.5878 (1)	−0.2576 (2)	0.3594 (1)	32 (1)	108 (4)	30 (1)	−23 (2)	−10 (1)	−5 (1)
Cl(4)	0.2878 (1)	−0.0350 (2)	0.4749 (1)	63 (2)	186 (4)	16 (1)	−32 (2)	−2 (1)	−5 (1)
C(5)	0.2542 (5)	0.0172 (7)	0.1478 (3)	60 (7)	76 (15)	19 (2)	−48 (8)	−1 (3)	−1 (5)
C(6)	0.3987 (4)	−0.0965 (7)	0.1979 (3)	41 (6)	66 (14)	23 (3)	−32 (8)	5 (3)	−7 (5)
C(7)	0.4099 (5)	−0.1128 (7)	0.2991 (3)	40 (6)	75 (14)	23 (3)	−31 (8)	−4 (3)	−4 (5)
C(8)	0.2764 (5)	−0.0155 (7)	0.3512 (3)	59 (7)	83 (15)	17 (2)	−43 (8)	−3 (3)	−1 (5)
C(9)	0.1340 (5)	0.0977 (7)	0.3001 (3)	41 (6)	57 (14)	19 (3)	−22 (8)	3 (3)	−7 (5)
C(10)	0.1241 (5)	0.1122 (7)	0.2007 (3)	41 (6)	52 (14)	21 (3)	−29 (8)	−3 (3)	−3 (4)
C(11)	−0.0410 (5)	0.2385 (7)	0.1690 (3)	54 (6)	83 (15)	30 (3)	−41 (8)	1 (4)	0 (5)
C(12)	−0.0257 (5)	0.2146 (8)	0.3344 (3)	52 (6)	85 (15)	21 (3)	−39 (8)	−2 (3)	−1 (5)
O(13)	−0.1061 (4)	0.2964 (6)	0.0907 (2)	63 (5)	170 (12)	25 (2)	−34 (6)	−10 (3)	−1 (4)
O(14)	−0.0718 (4)	0.2468 (6)	0.4125 (2)	70 (5)	143 (11)	25 (2)	−39 (6)	12 (3)	−10 (4)
O(15)	−0.1248 (3)	0.2929 (5)	0.2517 (2)	34 (4)	116 (11)	25 (2)	−19 (5)	5 (2)	−8 (3)
	Positional parameters for $C_{10}D_8$			Anisotropic temperature factors for $C_{10}D_8$					
	x	y	z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
C(16)	0.0691 (5)	0.6551 (8)	0.1580 (3)	66 (7)	99 (15)	31 (3)	−52 (9)	−9 (4)	−3 (5)
C(17)	−0.0505 (5)	0.7398 (8)	0.2180 (4)	48 (7)	107 (16)	44 (3)	−39 (9)	−10 (4)	2 (6)
C(18)	−0.0232 (5)	0.7117 (8)	0.3192 (4)	59 (7)	99 (15)	36 (3)	−42 (8)	15 (4)	−15 (5)
C(19)	0.1259 (5)	0.5972 (8)	0.3589 (3)	74 (7)	118 (16)	20 (3)	−62 (9)	10 (3)	−7 (5)
C(20)	0.4072 (5)	0.3903 (8)	0.3377 (4)	59 (7)	100 (15)	34 (3)	−41 (9)	−23 (4)	16 (5)
C(21)	0.5274 (5)	0.3070 (8)	0.2777 (4)	43 (7)	88 (16)	60 (4)	−31 (8)	−8 (4)	5 (6)
C(22)	0.4987 (6)	0.3355 (8)	0.1770 (4)	71 (8)	108 (16)	54 (4)	−55 (9)	23 (4)	−20 (6)
C(23)	0.3509 (6)	0.4470 (8)	0.1369 (4)	89 (8)	94 (15)	34 (3)	−72 (9)	12 (4)	−13 (5)
C(24)	0.2244 (5)	0.5358 (8)	0.1970 (3)	60 (6)	63 (14)	24 (3)	−47 (8)	1 (3)	−3 (5)
C(25)	0.2525 (5)	0.5084 (8)	0.2984 (3)	44 (6)	78 (14)	23 (3)	−35 (8)	−1 (3)	−5 (5)

[a] Estimated standard deviation of the last significant figure is given in parentheses. [b] Anisotropic temperature factors are of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

tained is limited, probably by the presence of the heavy silver atoms. Structural data are also available for the $Cr(CO)_3$ complex of naphthalene[7] but the standard deviations of the carbon–carbon distances in this complex are about 0.03 Å.

Several spectroscopic investigations[8-10] have been undertaken of the charge transfer complex of naphthalene and tetrachlorophthalic anhydride (TCPA) in which naphthalene acts as a donor and TCPA as an accepter. These studies of the absorption and phosphorescence spectra were carried out with glassy samples at low temperature. While a patent[11] has been obtained for separation of naphthalene from petroleum fractions by precipitation of the TCPA complex, little spectroscopic information is available for the crystalline complex. The phosphorescence microwave double resonance (PMDR) technique developed by El-Sayed, Gossett, and Leung[12] provides detailed information concerning the origin of phosphorescence in charge transfer complexes of this type. This technique makes possible the determination of the orientation of the magnetic axis of the emitting species in a single crystal sample. Combined with an X-ray structure determination such an investigation can yield the relationship between the emitting species and the molecular species in the crystal. The naphthalene–TCPA complex is a good candidate for such an investigation since its triclinic symmetry simplifies the interpretation of the experimental results.

In an effort to provide accurate structural parameters for a molecular complex of naphthalene and at the same time furnish a structural basis for a single crystal PMDR study of a charge transfer complex, the X-ray crystal structure determination of the naphthalene–TCPA complex was undertaken. To avoid errors associated with large thermal motion and disorder, the X-ray data were collected at −153°.

Experimental Section

Light-yellow crystals of the charge transfer complex were obtained when equimolar portions of $C_{10}D_8$ and TCPA were mixed in methyl methacrylate, heated, and allowed to cool slowly. The crystals grew in needles along the *b* axis. Preliminary oscillation and Weissenberg photographs of these crystals exhibited triclinic Laue symmetry. Intensity data were collected at −153° on a Syntex $P\bar{1}$ autodiffractometer modified for low temperature data collection.[13] In this configuration the scintillation counter was located 19.5 cm from the crystal. The single crystal chosen for X-ray investigation was cleaved from a large needle-shaped crystal. The perpendicular distances between the 110, 101, and $10\bar{1}$ faces of the fragment were 0.045, 0.039, and 0.022 cm, respectively. The crystal was mounted with the $[1\bar{1}1]$ direction roughly parallel to the φ axis of the diffractometer. After optical alignment, 15 reflections were carefully centered with crystal monochromatized Mo Kα (λ 0.7107 Å) radiation. Least-squares refinement of the lattice parameters based on these reflections gave a = 10.042 (5), b = 6.701 (2), c = 13.872 (9) Å, α = 86.34 (4), β = 90.82 (5), and γ = 59.63 (3)° at −153°. After data collection, the crystal was realigned at room temperature and these same 15 reflections were recentered. The room temperature (22°) lattice parameters obtained were a = 10.142 (6), b = 6.874 (5), c = 14.03 (1) Å, α = 86.80 (8), β = 90.76 (7), and γ = 59.49 (6)°. The room temperature density of 1.66 g/cm³ determined by flotation in mixed solvents is in good agreement with the calculated room temperature density of 1.667 g/cm³ for Z = 2. The intensity of all independent reflections with $2\theta \leq 50°$ was measured with a θ–2θ scan technique. Each peak was scanned from 1.5° below the 2θ for Mo Kα_1 to 1.5° above the 2θ for Mo Kα_2 at a scan rate of 2.4°/min. Background was measured at each end of the scan with a ratio of total background count time to scan time of 0.8. The intensities of three test reflections were monitored every 100 reflections. The intensity decreases of less than 5% in each case did not warrant a correction to the observed intensities. A calculation[4] of trial absorption corrections for a sampling of reflections (μ = 2.27 cm^{-1}) varied from 0.96 to 0.98 (comparable to the random error in the intensities), and consequently,

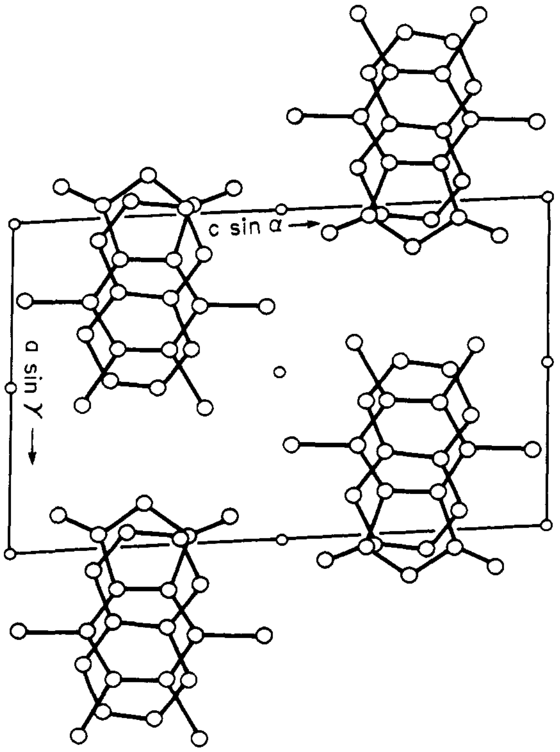

Figure 1. Packing diagram of the triclinic unit cell of the naphthalene-TCPA complex viewed down the b axis.

Table II. Positions Assigned to Deuterium Atoms[a]

Number	x	y	z
16	0.0488	0.6757	0.0862
17	− 0.1589	0.8225	0.1893
18	− 0.1116	0.7745	0.3628
19	0.1462	0.5765	0.4307
20	0.4273	0.3700	0.4095
21	0.6356	0.2252	0.3066
22	0.5871	0.2734	0.1334
23	0.3308	0.4673	0.0651

[a] The atom number refers to the carbon to which it is attached. All deuterium atoms were assigned an isotropic temperature factor of 3.0 Å² and a C–D distance of 1.0 Å.

no absorption correction was applied to the X-ray intensity data. For each reflection, the intensity, I, and its standard deviation, $\sigma(I)$, were calculated from the equations $I = \mathrm{CT} - (t_c/t_b)(B_1 + B_2)/2$ and $\sigma(I) = (\sigma_s^2 + (0.04I)^2)^{1/2}$ where CT is the total integrated count, t_c is the counting time for the scan, t_b is the counting time for each background, B_1 and B_2 are the background counts on each side of the scan, and σ_s is the standard deviation in the intensity as obtained from counting statistics. The data were corrected for Lorentz polarization effects and reduced to $|F_o|$'s. The 2043 data with $|I| \leq 3\sigma(I)$ were considered observed and used in subsequent solution and refinement of the structure.

Determination and Refinement of the Structure. The positions of the four independent chlorine atoms were deduced from a three-dimensional Patterson function based on the observed data. Successive Fourier difference syntheses were used to locate all the other nondeuterium atoms. Least-squares refinement of positional and isotropic temperature factors for the nondeuterium atoms converged to $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.087$ and $R_w = (\Sigma w||F_o| - |F_c||^2/\Sigma_w|F_o|^2)^{1/2} = 0.091$ where $w = 1/(\sigma F_o)^2$. With deuterium atoms included in calculated positions (C–D; 1.0 Å), refinement of positional and anisotropic thermal parameters for the nondeuterium atoms converged to $R = 0.048$ and $R_w = 0.046$. The scattering factors of Hanson et al.[15] were used for all nondeuterium atoms. The hydrogen scattering factors obtained by Stewart et al.[16] were used for deuterium. The final positional and thermal atomic parameters of the nondeuterium atoms together with their standard deviations are given in Table I, and calculated positions for the deuterium atoms are tabulated in Table II.

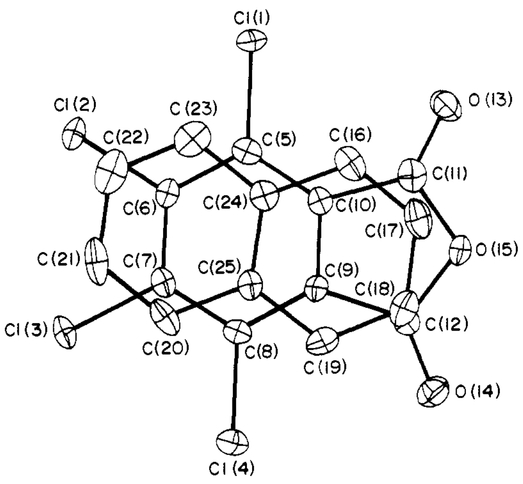

Figure 2. Molecular structure of the π complex of naphthalene and TCPA with 50% probability thermal ellipsoids and the numbering system used in this investigation.

Description and Discussion of the Structure. The structure of the complex consists of columns of alternately stacked molecules of naphthalene and TCPA parallel to the b axis of the crystal. The mean planes of the naphthalene and TCPA molecules can be expressed by

$$-0.49462X - 0.86865Y + 0.02828Z = 4.80938$$

and

$$-0.50844X - 0.86069Y + 0.02645Z = 1.48306$$

respectively, where X, Y, and Z are the ångstrom coordinates with respect to the crystal axes, a, (c^*xa), and c^*. The normals to these planes make angles of 1.8 and 1.5° respectively with the crystallographic b axis. Figure 1 shows the packing of the molecules in the unit cell. This packing arrangement is similar to that observed in the complex of naphthalene and tetracyanobenzene.[2] Figure 2 shows the numbering system employed in this study and the 50% probability thermal ellipsoids. The ellipsoids give no evidence of the disorder observed in other charge transfer complexes of naphthalene.[2,3]

Absence of any disorder and the reduced thermal motion at 120°K allow quite accurate determination of the structural parameters of this complex. Such a determination furnishes an opportunity to compare detailed structural parameters of the component molecules in a charge transfer complex with those observed in the pure solids, and in the case of naphthalene with those observed in the gas phase. Observed bond distances and angles for the naphthalene and TCPA molecules are shown in Figure 3. The shortest intermolecular distances between naphthalene and TCPA are C(18)-C(20) = 3.34 Å, C(7)-C(20) = 3.35 Å, and Cl(2)-C(22) = 3.39 Å.

Only small deviations from planarity are observed for either molecule. For the naphthalene molecule the largest deviation of 0.007 Å is probably not significant. Likewise all the chemically equivalent bond lengths in the naphthalene molecule differ from the mean by less than the estimated standard deviation in the individual observations. In Table III the means of the chemically equivalent bond lengths are compared to those obtained from a crystallographic study of naphthalene[4] and with those from a gas phase electron diffraction study.[5] The crystallographic data for naphthalene at room temperature were refined with corrections for rigid body thermal motion. No such corrections were made in the refinement of the naphthalene-TCPA complex, but at −153° the motion is reduced to the point where such corrections would be quite small. To within the estimated experimental uncertainties, the observed bond lengths of naphthalene in the TCPA complex, in the pure crystal, and in the gas phase are identical.

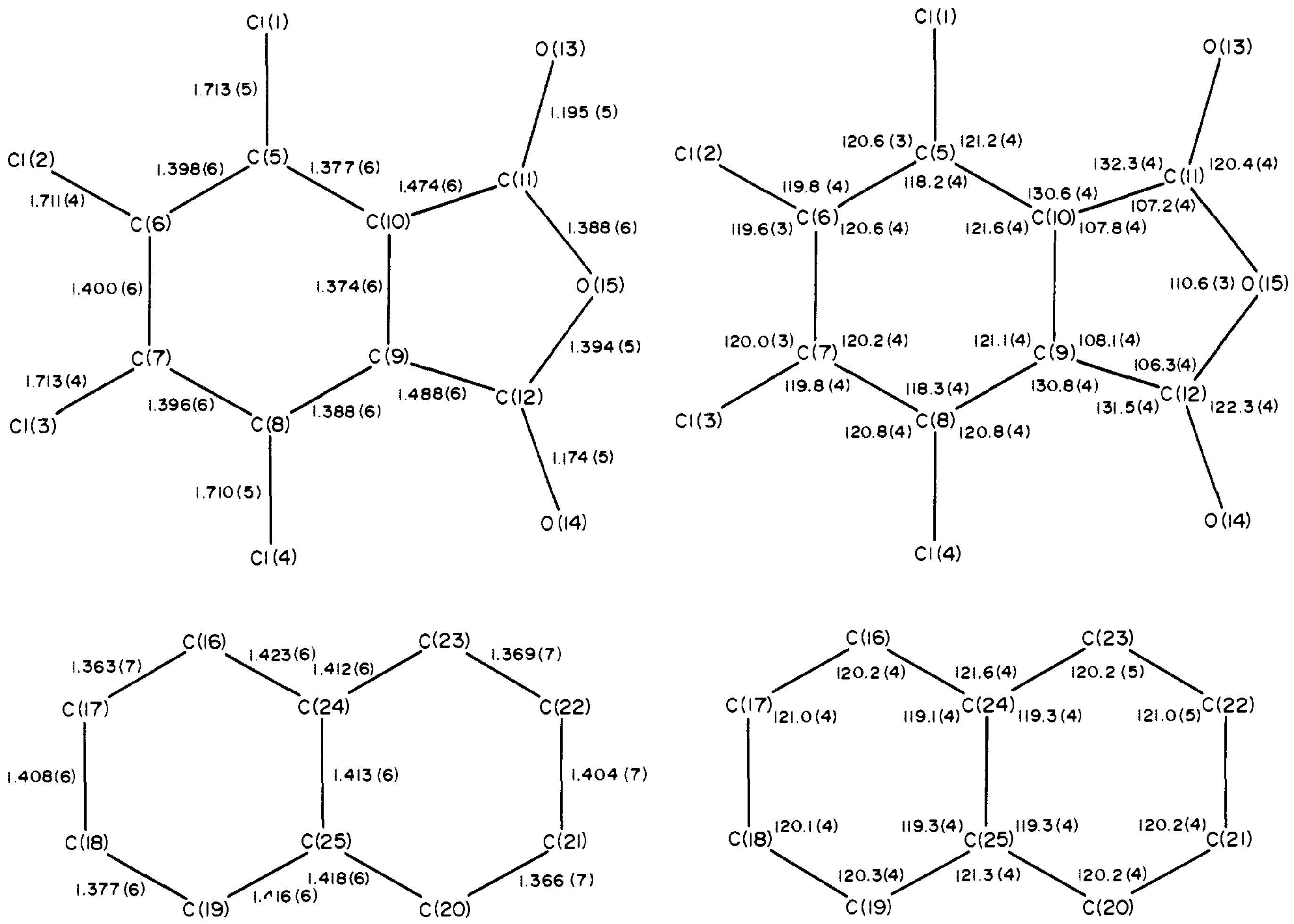

Figure 3. Bond distances and angles in the naphthalene and TCPA molecules.

Table III. A Comparison of Interatomic Distances for Naphthalene in Its TCPA Complex, in Crystalline Naphthalene,[4] and in the Gas Phase[5]

	Naphthalene-TCPA[a]	Crystalline naphthalene	Gas phase electron diffraction
C(24)-C(25)	1.413 (6)	1.418 (5)	1.422 (7)
C(16)-C(24)	1.417 (6)	1.421 (5)	1.421 (4)
C(16)-C(17)	1.369 (7)	1.364 (5)	1.371 (9)
C(17)-C(18)	1.406 (6)	1.415 (5)	1.412 (14)

[a] Average of chemically equivalent distances; estimated standard deviations of individual observations are given in parentheses.

Table IV. A Comparison of Interatomic Distances of TCPA in Its Naphthalene Complex and in Crystalline TCPA[16]

	Naphthalene-TCPA[a]	TCPA[b]
C(11)-O(13)	1.184	1.186
C(11)-O(15)	1.391	1.401
C(10)-C(11)	1.481	1.500
C(5)-C(10)	1.382	1.382
C(6)-C(5)	1.397	1.402
C(7)-C(6)	1.400	1.380
C(5)-Cl(1)	1.712	1.666
C(6)-Cl(2)	1.712	1.698

[a] Individual standard deviations range from 0.004 to 0.006. [b] Individual standard deviations range from 0.013 to 0.022.

The TCPA molecule in the charge transfer complex shows only slightly larger distortions from planarity than observed for the naphthalene molecule. The largest deviation from the mean plane is 0.028 Å for the O(15) atom. Chemically equivalent distances in the TCPA molecule differ from the mean by less than twice the estimated standard deviation. Table IV compares the mean bond distances in the TCPA molecule of the naphthalene-TCPA complex with those observed in crystalline TCPA.[17] In the TCPA structure, deviations from planarity as large as 0.08 Å were observed. These significant deviations probably result from greater nonbonding Cl-Cl interactions in pure TCPA. The estimated standard deviations in the bond distances in the TCPA structure are about four times greater than those obtained from the complex, but to within the experimental uncertainty all corresponding C-C and C-O bonds in these structures are the same length. The slightly shortened C-Cl bonds observed in the room temperature TCPA structure almost certainly result from the larger thermal motion. On the basis of the TCPA structure Rudman[17] observed no significant difference in the lengths of the two C-Cl bonds in TCPA although NQR studies suggested that such a difference might exist. In the current study these two distances were both observed to be 1.712 (4) Å.

It has been demonstrated that any distortion in the molecular geometry which occurs on formation of the naphthalene-TCPA complex must be smaller than the accuracy to which these parameters have been measured. It is also clear that in the structural determinations of molecular charge transfer complexes, where thermal motion of one of the component molecules is often large at room temperature, a high degree of experimental accuracy can be achieved with low temperature data collection.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, refering to the code number JACS-75-3000.

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The Electronic Structure of the Criegee Intermediate. Ramifications for the Mechanism of Ozonolysis

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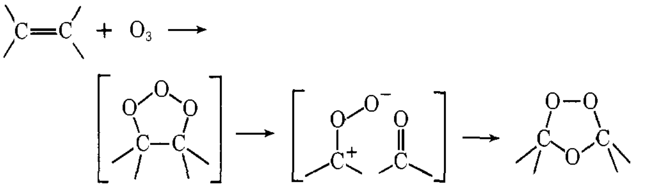
Abstract: Generalized valence bond (GVB) and configuration interaction (CI) calculations using a double ζ basis set have been carried out on methylene peroxide (H_2COO), the reactive intermediate in the Criegee mechanism for ozonolysis of olefins. The ground state of methylene peroxide (using an open geometry) is shown to be a singlet biradical rather than a zwitterion. A strong analogy between methylene peroxide and its isoelectronic counterpart, ozone, is developed. The calculations also show that the ring state of methylene peroxide is 1 eV lower than the open form. Moreover, the ring state may reopen to give the dioxymethane biradical. The ab initio results are combined with thermochemical data in order to analyze the stability of the Criegee intermediate as well as the possible modes of reaction in ozonolysis. With regard to ozonolysis in solution, the mechanism for epoxide formation is elucidated and the possible role of methylene peroxide rearrangement to dioxymethane is considered in interpreting the ^{18}O isotope experiments. With regard to ozonolysis in the gas phase, the production of many of the chemiluminescent species observed by Pitts and coworkers is explained. The production of reactive radicals such as OH and HO_2 in the course of ozonolysis, which may have important consequences for understanding the generation of photochemical air pollution, is also delineated.

I. Introduction

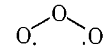
The reaction of ozone and olefins (in solution) with its puzzling set of products has intrigued chemists for years.[2-4] More recently, the corresponding gas phase reaction has come under scrutiny as an important link in the chain of photochemical smog production.[5] The isolation in solution of 1,2,4-trioxolanes rather than 1,2,3-trioxolanes from ozone-olefin reaction mixtures and the incorporation of foreign aldehydes in the 1,2,4-trioxolanes led Criegee[6] 25 years ago to propose the following mechanism



1 2 3

Since then a great deal of experimental work has substantiated the Criegee mechanism as either the predominant or at least a major pathway for ozonolysis in solution.[3,4,7-9] However, no definitive mechanistic studies have as yet been performed on gas phase ozonolysis.

Recent extensive ab initio calculations[10,11] have shown that ground state ozone is basically a singlet biradical (**4**)



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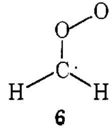
rather than the resonance of two VB zwitterions (**5**)

5

as often proposed. In fact, the state that corresponds most closely to **5** is about 5 eV higher than the ground state![10] Since the Criegee intermediate, methylene peroxide (**2**), is isoelectronic to ozone, we expected it to have an analogous ground state and hence to correspond essentially to a singlet biradical (**6**) rather than a zwitterion (**2**) as is normally assumed. In order to establish the electronic structure of methylene peroxide (**2** or **6**) and to investigate the role of



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