# DONOR - ACCEPTOR INTERACTION OF FREE RADICALS WITH ORGANIC ELECTRON ACCEPTORS

A. A. Kuznetsov, S. N. Novikov, and A. N. Pravednikov UDC 543.422.27:541.49:541.515

Charge-transfer complexes (CTC) play an important role in many organic reactions. It has been repeatedly pointed out that they may also participate in free-radical reactions [1-5]. Their comparatively high electron affinities and ionization potentials suggest that certain free radicals should show appreciable activity in donor-acceptor reactions. On the other hand, complexing with solvents and substrate must markedly affect radical reactivity [1-4].

Most of the reports of the formation of radical CTC have been based on kinetic data which can, at best, give only indirect evidence of donor-acceptor complexing. Although the formation of such complexes has, in many instances, been confirmed by spectrometric studies [2, 6-8], these data are too limited to serve as a basis for general conclusions concerning the relation between free-radical structure and ability to form CTC. The present work was a study of CTC of the nitroxyl and hydrocarbon radicals of the phenylmethyl and cyclopentadienyl series with organic acceptors. The acceptors investigated here were maleic anhydride (MA), duroquinone (DQ), p-benzoquinone (BQ), pyromellitic dianhydride (PDA), trinitrobenzene (TNB), 2,5-dichlorobenzoquinone (DCQ), chloranil (CA), tetracyanoethylene (TCE), tetracyanoquinodimethane (TCQM), and 2,3-dicyano-5,6-dichlorobenzoquinone (DDC).

#### EXPERIMENTAL

These studies were carried out through low-temperature electronic spectroscopy [9], a highly sensitive method for detecting weak donor-acceptor interaction, and one which has been successfully applied to detect CTC formation in cases where the usual methods of investigating complexing in solution breakdown. The sensitivity of the method results from the high concentration of the CTC components in sublimed films, and from the fact that the complexing equilibrium is shifted to the CTC side at low temperatures. Here one builds up a high concentration of reactive particles on a cold surface, and then uses spectroscopic methods to follow the reactions of these particles as the surface is warmed to  $\sim 20^{\circ}$ C.

Charge-transfer complexes with 2,2,6,6-tetramethylpiperidin-l-oxyl (TMPO) were obtained by the simultaneous sublimation of radical and acceptor onto a quartz spectroscopic window which was cooled with liquid nitrogen. Charge-transfer complexes of the pentaphenylcyclopentadienyl (PPhCPD) radical were prepared in the same way.

Triphenylmethyl (TPhM) was prepared by rapid vaporization of a dilute solution of the dimer of compound (I) onto the surface of the spectroscopic window at --196°C. Here, dissociation into radicals occurs during passage into the gaseous phase. The less stable dimethyl-phenylmethyl (DPhM), 2-phenylisopropyl (cumene, Cum), and benzyl radicals were prepared by hydrolysis of 1,1,2,2-tetraphenylethane, 2,3-dimethyl-2,3-diphenylbutane, and tetrabenzyltin at 600-700°C, the decomposition products being rapidly condensed on the cold surface. Pyrolysis was carried out in a capillary heated with a Nichrome winding, working in a vacuum of  $10^{-3}$  mm with the spectrometer window 20 mm from the heating zone. The temperature in the heating zone was measured with a thermocouple. The radical concentration was determined in a similar manner, the radicals being condensed on the end of the capillary of the ESR cell. The ESR spectra were obtained with a RA-100 spectrometer. The electronic spectra were obtained with a Perkin-Elmer-450 spectrometer. The methods of low-temperature IR spectroscopy were used for radical identification in some cases.

The TPhM solutions were made up in degassed solvents. The operations involved in preparing the solutions and dosing with the various acceptors were carried out in vacuum.

L. Ya. Karpov Physicochemical Institute, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 297-303, February, 1979. Original article submitted August 25, 1977.

The dimer of compound (I) was prepared by shaking Ph<sub>3</sub>CCl with mercury in degassed ben-The Ph<sub>3</sub>CC1 has been recrystallized from heptane containing activated charcoal. Reaczene. tions were carried out in a hermetically seal system consisting of a reaction flask and an ampul receiver joined to the latter through a glass filter. The colored liquid left after settling was transferred to the ampul, the benzene condensed back into the flask, the product extracted 4-5 times, the benzene distilled off, the ampul sealed and the dry residue held in vacuum for 15 h. The product (I) was obtained as a cream-colored powder with a melting point of 150°C. Dosing with this compound was carried out in an atmosphere of argon. The 1,1,2,2tetraphenylethane was recrystallized from CHCl3 and had a melting point of 210°C. The 2,3dimethyl-2,3-diphenylbutane was prepared by dehydrodimerization of cumene with acetyl peroxide, following the method of [10]. The PPhCPD and pentaphenylcyclopentadiene were synthesized by the procedures of [11]. The cyclopentadienyl radical was prepared by pyrolysis of tetracyclopentadienyltin, with rapid condensation of the vapors onto the surface at -196°C. The TMPO was purified by vacuum sublimation. The quinone-type electron acceptors were purified by recrystallization from alcohol or benzene solution with subsequent vacuum sublimation. The TCE was recrystallized from chlorobenzene, and sublimed in a  $10^{-1}$  mm vacuum onto an icecooled surface. The TCQM was recrystallized from purified CH<sub>3</sub>CN, and the TNB from alcohol. The MA had been recrystallized from absolute CHCl3 solution and sublimed. The PDA was recrystallized from benzene solution, and vacuum sublimed twice.

## DISCUSSION OF RESULTS

The electronic spectra of sublimed TMPO-electron-acceptor mixtures showed wide, longwave, absorption bands which were missing from the component spectra. Values of  $\lambda_{\text{max}}$  for these bands are given in Table 1. These were assumed to be bands for charge transfer (CT) from the TMPO to the acceptor, the band energy varying linearly with the electron affinity of the acceptor (Fig. 1). A study of TMPO-acceptor interaction in solution and at room temperature showed that CTC were formed only with TCE and DDC, the two strongest acceptors. It is possible that the steric hindrances opposing complex formation are balanced against the charge-transfer forces, the latter playing a central role in the formation of CTC with these acceptors. Evaluated by the Benesi-Hildebrand method, the equilibrium constant for the complexing of TMPO with TCE in chloroform solution proved to be equal to 5.6 liters/mole. This is in line with the K<sub>e</sub> value of 4.0 liters/mole reported [7] for charge-transfer complexing of the di-tert-butylnitroxyl radical with TCE. A study of the interaction of TMPO with acceptors in CH<sub>3</sub>CN, a polar solvent, showed complete charge transfer from the radical to the acceptor with the formation of the DDC radical ( $\lambda_{max}$  590, 525 nm), the TCE radical (417 nm), or the TCQM radical (750, 850 nm). Special interest attaches to the question as to whether the unpaired electron is involved in the complexing process. It has been suggested that the donor orbital is the unpaired electron orbital of oxygen. The same conclusion has been advanced [12] on the basis of studies of nitroxyl radical complexes with Lewis acids. Here the presence of an unpaired electron in the molecule would certainly reinforce the donor activity. Thus the value of the ionization potential, a rough measure of electron-donor capacity, is 7.4 eV for 2,2,6,6-tetramethyl-4-oxo-piperidin-1-oxyl and 8.5 eV for the corresponding hydroxylamine.

In order to bring out the role played by the unpaired electron in radical complexing, a study was made of the CTC of radicals with simple electronic structures, more particularly TPhM, DPhM, and Cum, alternating hdyrocarbon radicals of the phenylmethyl type. The literature contains no information on radical CTC which do not contain a heteroatom.

The radicals were identified by the characteristic absorption bands in their electronic spectra (TPhM, 513 nm; DPhM, 335 nm; Cum, 324 nm; benzyl, 320, 311, 307 nm), each of which disappeared on heating the sample to room temperature. At -196°C, the ESR spectra of the TPhM and DPhM radicals were singlets, narrow in the one case, and wide in the other. The fact that our DPhM radical spectrum differed from that described in [13] could have been due to differences in the experimental conditions. The Cum spectrum was similar to that described in [14]. The benzyl radical spectrum had the form of a wide singlet. Radical concentrations were determined from the integral intensities of the ESR signals, the respective values being 70, 20, and 5% for the TPhM, DPhM, and Cum radicals.

At -196°C, the electronic spectra of sublimed mixtures of electron acceptor and TPhM, DPhM, or Cum radicals showed the bands for the system components and new absorption bands lying in the near IR and visible region of the spectrum. These new bands, and the radical

f Complexes of Radicals		
the Spectra of		
Bands in		
harge-Transfer		
for the C	rs	
Ελ <sub>max</sub> (nm)	ron Acceptc	
Values o	ganic Electi	
TABLE 1.	with Org	

				4	"srondana	anu electr	on annunes,	ev		
Radical	MA	g	TNB	ğ	PDA	DCQ	CA	TCQM	TCE	DDC
	0,5	0,6	0,7	0,8	0,85	1,1	1,37	1,7	1,8	1,9
2,2,6,6-Tetramethylpiperidin-1-oxyl	1	. 1	1	490	490	550	670	67	725	8/15
TriphenyImethyl	590	660	730	780	880	1060	1490	770 b, 870b	$410^{\mathbf{S}}, 430^{\mathbf{C}}, 1450$	720 <sup>d</sup> 1320 <sup>d</sup> , 590 <sup>b</sup> , 525 <sup>b</sup> ,
DiphenyImethyl	1	I	620	725	775	940	1150	4	1400d, 440c	¢3
Cumene	430 sh	8	480 sh	ಭ	560 sh	585	685	ß	730	¢
Pentaphenylcyclopentadi enyl	1	1	1	I	1	1	700 sh	840	850	1000
Pentaphenylcyclopentadiene	1	1	500	500	500	550	650	I	022	920
	-	:		ľ	•					

CTC formation not detected, possibly because of rapid chemical reaction. Anion-radical acceptor band.

. م. ۲. ۳. ۳

Cation band. Band departing from the general  $\nu$  vs  $E_{\mathcal{C}}$  relation.



Fig. 1. Variation of the energy of the chargetransfer band of radical complexes with the electron affinity: 1) triphenylmethyl; 2) diphenylmethyl; 3) cumene; 4) 2,2,6,6-tetramethylpiperidin-1-oxyl; 5) pentaphenylcyclopentadienyl.

bands, disappeared when the sample was heated. Figure 2 shows spectra for the TPhM-CA system which are typical of radical CTC's of this type. Values of  $\lambda_{max}$  are given in Table 1. The band energy was linearly related to the electron affinity in each of these three series. This was indication that it was here a matter of charge transfer complexes. The failure of new bands to appear in the benzyl radical spectra was probably due to the fact that the radical and the acceptor reacted even before the pyrolysis products condensed on the cold surface.

The position of the charge transfer band in these spectra is rather unusual for the  $\pi - \pi$  type radical complexes, suggesting that the donor properties are quite marked in these compounds. Special experiments proved that these were indeed radical complexes and not complexes which had been formed with the intermediate or final pyrolysis products. In these experiments, the radical-containing products from the pyrolysis of the DPhM and Cum dimers were heated to room temperature and then sublimed, either onto the capillary of the ESR cell (together with the acceptor) or onto the liquid-nitrogen-cooled window of the spectroscope. Sublimed films obtained in this manner gave no ESR signal; at -196°C their electronic spectra showed a band at 400-500 nm which was assigned to CTC's of the final pyrolysis products. This method of donor identification could not be applied in the case of TPhM, the spectra of the material obtained in the second sublimation showing a radical regeneration band with  $\lambda_{max}$  513 nm. The band from the radical CTC band was still present here. The presence of the cyclohexadiene structure with its extended conjugated bond system suggested that dimer (I) would be a strong electron donor. It seems quite unlikely, however, that it would be a stronger donor than tetraphenylethylene or paraxylylene



(I)

whose complexes with TCE absorb at 600-700 nm [15]. In addition, complexing of (I) was not detected in studies on the interaction of TPhM and acceptors in solution. It is clear that only the TPhM radical could show such clearly expressed donor activity. This conclusion is supported by the fact that DPhM, whose dimer has the usual ethane structure, is also a strong electron donor.

The positioning of the curves in Fig. 1 is such as to indicate that the donor activity of the phenylmethyl radicals falls off in the order TPhM > DPhM > Cum. Such an ordering of donor activities would be consistent with values of the ionization potential (I) calculated by the MO LCAO method in the Pariser-Parr-Pople approximation, the respective values for the TPhM, DPhM, and benzyl radicals being 7.19, 7.34, and 7.76 eV. (The I value given is



Fig. 2. Electronic spectra of CTC of chloranil with tetraphenylmethyl (1), and with triphenylmethyl (2), recorded at  $-196^{\circ}C$ .

Fig. 3. Variation of the energy of the chrage-transfer band in the spectra of chloranil complexes with aromatic donors. The points cover data on CTC of the following radicals: 1) triphenylmethyl; 2) diphenylmethyl; 3) cumene.

for the benzyl radical rather than the cumene, since the effect of the  $CH_3$  group could not be taken into account in calculations of this type.) These calculations were undertaken because the literature does not contain experimental values, obtained for each of the radicals under the same conditions.

Figure 3 shows the variation of the energy of the charge transfer band of chloranilaromatic donor complexes with the ionization potential [16]. It can see that the points for the CTC of the TPhM, DPhM, and Cum radicals departed from the general relation, these radicals making up a special class of donors.

The charge-transfer bands in the TPhM-TCE, TPhM-DDC, and DPhM-TCE systems, those with most pronounced donor-acceptor properties, lie further in the shortwave region of the spectrum than would have been anticipated from the electron affinities and the character of the v vs  $E_{\alpha}$  relation, thus departing from the general rule. It should be noted that the spectra of these systems (and the TPhM-TCQM system, as well), obtained at -196°C, showed the following acceptor anion-radical bands: TCE<sup>+</sup> (2160 cm<sup>-1</sup>, in the IR spectrum), DDC<sup>-</sup> (590 nm), and TCQM<sup>+</sup> (770, 870 nm). The spectrum of the DPhM-TCE system showed not only the charge-transfer band, but also a band for the diphenylmethyl cation with  $\lambda_{max}$  440 nm. The appearance of such ion products was taken as evidence of complete electron transfer in these systems. It is possible that the bands which failed to fit the general relation arise from CTC of the acceptor cations or anion-radicals, or even from "reverse" charge transfer from the anion-radical to the cation [17].

A study of the interaction of TPhM with electron acceptors in chloroform solution at 20°C showed a rapid disappearance of the radicals, the ESR signal, and the band with  $\lambda_{max}$  513 nm in the electronic spectrum in almost every case. There was very little destruction of the radicals in systems containing MA, PDA, and TNB, the form of the spectrum remaining unchanged over several days. Even under these conditions, however, formation of CTC could not be detected. It is possible that failure to complex was due to the low equilibrium concentration of the TPhM (of the order of  $10^{-3}$  mole/liter), and to the fact that the complex-ing constant is much lower at 20°C than at -196°C. The presence of electron acceptors in the system had no effect on the ESR spectra. The interaction of TPhM with TCE, TCQM, and DDC in acetonitrile led to complete electron transfer to the acceptor, with the formation of a highly unstable anion-radical acceptor.

Tetracyanoethylene also complexes with the analogous triphenylmethane, diphenylmethane, and cumene molecules which do not have unpaired electrons, the charge-transfer bands in these compounds falling in the 350-400 nm region of the spectrum (cf. Fig. 2). The donor activities of these complexes are therefore comparable with that of benzene, while the donor activities of the radicals from that series are higher than essentially any aromatic compound (cf. Fig. 3). In order to obtain further information of the effect of the electronic structure on the donor properties of radicals, a study was made of the CTC of nonalternating hydrocarbon radicals of the cyclopentadienyl series. Attempts at preparing CTC of the unsubstituted cyclopentadienyl with  $\pi$  acceptors ended in failure. The electronic spectra of these systems showed a charge-transfer band which probably arises from the CTC of the product from the recombination of 9,10-dihydrofulvalene (II) radicals, or from recombination of the radicals of 1,5-dihydrofulvalene (III), its more stable isomer;  $\lambda_{max}$  670 nm for the CTC with CA.



In this connection, a study was also made of the stable CTC of PPhCPD. Beginning with CA, the electronic spectra of PPhCPD-strong acceptor mixtures each showed a typical chargetransfer band (cf. Table 1) whose energy was linearly dependent on the electron affinity (cf. Fig. 1). It is possible that similar bands appear in the spectra of radical complexes with weaker acceptors but are masked by the strong radical absorption in the visible region. It is also possible that complexes of this type are unstable, the antibonding orbital of the radical being lower, energy-wise, than the antibonding orbital of the acceptor. Complex formation was not detected in our studies on the interaction of PPhCPD with TCE in solution.

The corresponding hydrocarbon, pentaphenylcyclopentadiene, forms a series of CTC with various acceptors (cf. Table 1). Judging from the position of the CT bands, the donor activity of a radical CTC and a diene CTC, each with the same donor, must be about the same. This would be in line with the degeneracy of the higher filled radical orbitals, and with the fact that there is little difference in the values of the ionization potentials of the unsaturated radicals, on the one hand, and the dienes, on the other.

Comparison of the results of our studies on the CTC of alternating and nonalternating radicals, and the data on the CTC of the alternating radicals and the corresponding hydrocarbons, shows that the donor orbital responsible for the formation of alternating radical CTC with organic electron acceptors is high and partially filled. It is this orbital which carries the unshared electron.

## CONCLUSIONS

1. We have obtained direct experimental proof of the formation of CTC or organic electron acceptors and free hydrocarbon radicals, some of the alternating type (triphenylmethyl, diphenylmethyl, cumene) and some of the nonalternating type (pentaphenylcyclopentadienyl).

2. The donor orbital involved in the formation of alternating hydrocarbon radical CTC is high and partially filled; it carries the unpaired electron.

3. A CTC of the stable 2,2,6,6-tetramethylpiperidin-l-oxyl radical with organic electron acceptors has been prepared, and the constant for its complexing with tetracyanoethylene was determined.

## LITERATURE CITED

- 1. A. L. Buchachenko and O. P. Sukhanova, Usp. Khim., <u>36</u>, 475 (1967).
- 2. A. N. Prokof'ev, S. P. Solodovnikov, N. N. Bubnov, and N. G. Radzhabov, Izv. Akad. Nauk SSSR, Ser. Khim., 1664 (1969).
- 3. M. L. Khidekel', G. A. Razuvaev, E. I. Novikova, L. A. Smirnova, and A. P. Khrushch, Izv. Akad. Nauk SSSR, Ser. Khim., 1530 (1964).
- G. Henrici-Olive and S. Olive, Z. Phys. Chem. (Frankfurt), <u>B47</u>, 286 (1965); <u>B48</u>, 51 (1966); <u>B48</u>, 35 (1966).
- 5. A. N. Pravednikov and S. N. Novikov, Vysokomol. Soedin., A13, 1404 (1971).
- G. A. Abakumov, V. D. Tikhonov, and G. A. Razuvaev, Dokl. Akad. Nauk SSSR, <u>187</u>, 571 (1969).
- 7. J. Murata and N. Mataga, Bull. Chem. Soc. Jpn., <u>44</u>, 354 (1971).
- 8. S. Bhat and S. Kuroda, Bull. Chem. Soc. Jpn., <u>46</u>, 3585 (1973).
- 9. A. N. Pravednikov, I. E. Kardash, N. P. Glukhoedov, and A. Ya. Ardashnikov, Vysokomol. Soedin., <u>A15</u>, 349 (1973).
- 10. B. N. Moryganov and A. A. Emel'yanov, Uch. Zap. Gor'kovsk. Univ., 1953, 179.

11. K. Ziegler and B. Shnell, Lieb. Ann. Chem., <u>446</u>, 266 (1925).

12. B. M. Hoffman and T. B. Eames, J. Am. Chem. Soc., <u>91</u>, 5168 (1969).

13. V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben, Dokl. Akad. Nauk SSSR, <u>147</u>, 643 (1962).

- 14. J. Lin, K. Tsuji, and F. Williams, Trans. Faraday Soc., 64, 2896 (1968).
- 15. A. A. Kuznetsov, S. N. Novikov, I. E. Kardash, and A. N. Pravednikov, Zh. Fiz. Khim., 48, 2578 (1974).
- 16. R. Foster, Organic Charge Transfer Complexes, Academic Press, London-New York (1969).
- 17. Y. Sato, M. Kinoshita, and M. Sano, Bull. Chem. Soc. Jpn., 43, 2370 (1970).

THE INTERACTION OF 3-HYDROXYPHENOXYL AND

5-METHYL-3-HYDROXYPHENOXYL RADICALS WITH COPPER(II) IONS

I. V. Renge, I. V. Khudyakov, and M. Ya. Gubergrits

#### UDC 541.515:547.56:546.56-128

(1)

Various aromatic  $\pi$  radicals (e.g., the phenoxyl and the semiquinone) readily complex with transition-metal ions (especially copper ions), or reduce these ions through electron transfer [1, 2]. A study of complexes with radical ligands gives a new approach to the chemistry of the coordination compounds.

The reactions of phenoxyl and semiquinone radicals (ArO'), prepared from hydroquinone and pyrocatechol, with copper ions have been described in [1]. We have used flash photolysis to study the absorption spectra and kinetics of destruction of ArO' radicals obtained from resorcinol and 5-methylresorcinol in the presence of  $Cu^{2+}$  ions. A study of the photodestruction of 5-methylresorcinol (orcinol), and the kinetics of destruction of the corresponding ArO' radicals, is a matter of practical interest. Orcinol, the principal phenolic component of waste waters from shale treatment, undergoes various natural reactions under the action of sunlight and atmospheric oxygen.

#### EXPERIMENTAL

The absorption spectra and destruction kinetics of the various short-lived particles were studied in the flash photolysis system described in [3]. Light with wavelengths in excess of 185 nm was used for photoexcitation of the solution. Fresh portions of the solution were used in each excitation. The absorption spectra of the solutions were obtained with a Perkin-Elmer 402 spectrophotometer. The resorcinol used here had been subjected to threefold recrystallization from dichloroethane, and then vacuum sublimed; the orcinol dihydrate was first freed of moisture and then vacuum sublimed; the CuSO<sub>4</sub> was a cp grade material; the solutions were buffered with  $CH_3COOH$  and NaOH, and the pH checked with a pH-340 pH meter. Distilled water served as the solvent. In certain cases, the solutions were freed of oxygen by being pumped off at a pressure of  $10^{-5}$  torr. All measurements were made at  $\sim 20^{\circ}C$ .

## DISCUSSION OF RESULTS

<u>Flash Photolysis of Resorcinol and Orcinol</u>. Flash photoexcitation of oxygen-free solutions of resorcinol and orcinol  $(5 \cdot 10^{-4} - 3 \cdot 10^{-3} \text{ M}, \text{ pH } 2-4)$  led to the appearance of hydroxy-phenoxyl radicals (ArO<sup>\*</sup>) as short-lived intermediate reaction products. The photolysis of phenolic compounds proceeds according to the scheme

ArOH +  $h\nu$  —  $ArO' + e_{aq}^- + H^+$   $\rightarrow ArO' + H^ Ar = 3-HOC_aH_4$  (I),  $3-HO-5-CH_3C_6H_3$  (II)

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Institute of Chemistry, Academy of Sciences of the ESSR, Tallin. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 304-307, February, 1979. Original article submitted September 23, 1977.