Molecular Associations of Hydrazones of Heterocyclic Systems. XI

Paolo Bruni, Carla Conti, Elisabetta Giorgini, Eziana Maurelli and Giorgio Tosi*

Dipartimento di Scienze dei Materiali e della Terra,
Università degli Studi di Ancona,
Via Brecce Bianche, I-60131 Ancona, Italy
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Complexes of hydrazones of heterocyclic compounds with organic acceptors are investigated through the evaluation of spectroscopic and thermodynamic properties. Values of the formation constants and comparison between uv-visible and ft-ir determinations on liquid and solid phases indicate these systems are weak complexes. Contributions from hydrogen bonding and the effects of π-π^* or n-π^* transitions on the spectroscopic and thermodynamic properties of the complexes are discussed.

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Introduction.

Hydrazones behave as electron donors in molecular complexes (MC) with organic acceptors in a variety of solvents with the formation constants characterized by low values [1-3]. With moderately large acceptors, like 2,4,7-trinitrofluoren-9-one or (2,4,7-trinitro-9-fluorenylidene)-malononitrile, the formation of solid complexes has been reported [4].

In the investigation of the molecular associations between hydrazones with π^*-acceptors, it has been hypothesized that the C=N-N group can be considered the active donor center on the basis of spectroscopic and thermodynamic evaluations [5]. We have also reported that the presence of two donor centers diversifies the approaching mode of the acceptor molecule [6].

In this work complexes of hydrazones, bearing an heterocyclic moiety as an additional donor center, are investigated.

Results and Discussion.

We have used as donors hydrazones **1-10** and as acceptors 2,4,7-trinitrofluoren-9-one (TNF), (2,4,7-trinitro-9-fluorenylidene)malononitrile (DTF), 1,3,5-trinitrobenzene (TNB) and tetracyanoethylene (TCNE). The λ max of the complexes in solution, together with some values of the formation constants (K_f), are reported in Table 1, while, in Table 2, uv-visible and ir data are listed. The acceptors TNF and DTF formed solid complexes with all the donors **1-10**, while TNB gave an isolable complex only with the donor **10**, and tetracyanoethylene, after formation of a transient species, only gave tricyanovinyl adducts [7].

UV-Visible Results.

All the complexes show one or two bands in the visible region, in some cases as a shoulder, reported in Table 1. The overlapping and the broadness of the bands are responsible for some degree of uncertainty in the λ max values. Mass spectra at low energy fields, as well as thin layer chromatography, do not indicate the formation of any adduct but only the presence of the original reagents; these facts can be indicative of the absence, between the components, of interactions strong enough to be characterized by the above techniques [4,8,9]. These weak forces, together with lattice interactions, allow us to obtain solid complexes [4]. A 1:1 ratio was established by elemental analysis and by the Job continuous variation method [10].

Table 1

Formation Constants (K_f, ℓmol^{-1}, TNB as Acceptor, Chloroform, 20°) and Absorptions Maxima (λ max, nm) of Complexes of Donors 1-10 with TNB, TNF, DTF and TCNE in Various Solvents

Donor	TNB		TNF			DTF		TCNE	
	K_f	$CHCl_3$	Cy [a]	$CHCl_3$		$CHCl_3$		CCl_4	Bz [b]
1		512	508	530	650	620	780	775	832
2	1.24±0.28	540	532	550	692	688	840	718	875
3		490	464	498	608		752	770	760
4	0.75±0.68	510	792	498	616	528	764	835	827
5	0.52±0.35	475	465	484	610	540	718	765	752
6	1.45±0.40	502	496	498	610	530	760	844	826
7		498	[c]		570	748	796	685	697
8		470	452	468	562		680	760	750
9		520	[d]	[d]		[d]		NO MC	NO MC
10		551	[d]	[d]		664	884	880	897

[a] Cyclohexane. [b] Benzene. [c] Donor **7** is not soluble in cyclohexane. [d] The complex was not soluble.

We were unable to determine the λ max of all the complexes in an unique solvent due to the low solubility, instability and extinction coefficients of some the reactants and adducts. Spectra in the visible region of complexes of TNF and, in some cases, of DTF show two new bands with respect to the reactants. As expected from the π-acid strengths of the four acceptors (TCNE > DTF > TNF > TNB), a red shift of the λ max was seen in going from TNB to TCNE complexes [11,12].

The overlapping of the bands and the low solubility of complexes of DTF or TNF as well as the reactivity of the ones of TCNE, limited the evaluation of the formation constants to complexes of TNB. Furthermore, due to stability and solubility problems, quantitative measurements were restricted to the systems **2**, **4**, **5**, **6** and **8**/TNB.

Table 2

Melting Points (°C) Infrared (cm^{-1}) and UV-Vis (nm) Data for Solid Complexes of Hydrazones **1-10** with TNF(I), DTF (II) and TNB (III)

Compound	mp	IR							UV-Vis							
		NH		C=N	C=O	C=N	NO_2									
		Heterocycle	Hydrazone				Asymmetrical	Symmetrical								
I					1731		1553, 1543, 1519	1370, 1359, 1344								
II				2230, 2222			1548, 1538, 1525	1360, 1347								
1		3421-8, 3404	3311			1575										
1/I	168	3438-28, 3394	3318-07		1717		1549, 1542, 1525	1372, 1344		530	592	672	744	798	861	
1/II	179	3428 b	3315	2228, 2221		1576	1558, 1542, 1528	1343		492	592	676				
2		3390				1576										
2/I	159	3393			1721	1576	1542, 1529	1362, 1336		544	596	684	742	796		
2/II	173	3389 b, 3357 b		2230		1576	1558, 1541, 1526	1367, 1345	488		596	684	748	796	832	
3			3318			1577										
3/I	146		3301		1728	1575	1554, 1543, 1525	1359, 1347, 1344		548	600	640	744			
3/II	180		3315, 3248	2227			1557, 1543, 1533	1365, 1342	490		594	682	740	794	856	
4						1578										
4/I	126				1728		1538, 1524	1372, 1362, 1343		548	580	698	732			
4/II	142			2229			1545, 1533	1365, 1359, 1343	488		588	680	738	792	860	
5			3325			1579										
5/I	136		3311		1732	1579	1553, 1543, 1520	1371, 1360, 1345		528	576	672	740			
5/II	178		3310, 3241	2227		1576	1559, 1542, 1535	1367, 1359, 1343	504	548	604	688	748	800	860	
6						1576										
6/I	132				1731		1557, 1543, 1525	1371, 1361, 1345		550	592	696	745			
6/II	175			2227		1572	1547, 1531, 1526	1369, 1342-5	490	540	596	680	748	796	832	
7			3225, 3183 b			1568 b										
7/I	138		3325, 3321, 3115, 3181		1733-21	1577	1542, 1526	1373, 1359, 1345		548	602					
7/II	183		3314	2229		1573	1547, 1534, 1527	1359, 1347 (43)	490		600	684	748	796	826	
8						1580										
8/I	150				1728	1579	1545, 1525	1372, 1354, 1342			582	668				
8/II	197			2227		1580	1558, 1546, 1533	1372, 1353, 1341	492	536		672		792		
9		3425, 3386	3285-1			1571										
9/I	204	3391 b	3322		1721	1571	1542, 1526	1373, 1359, 1343			584		752			
9/II	194	3424 b, 3383 b	3315	2224		1572	1554, 1544, 1534	1358, 1342	488	536	596		746	790	828	
10		3434 b, 3286 b				1574										
10/I	255	3450, 3370 b			1729	1574	1543, 1525	1371, 1359, 1343			572		740			
10/II	239	3403 b		2226		1576	1543, 1535, 1527	1369, 1357, 1343	498	544	600	684	746	808	832	872
III							1558, 1541, 1508	1387, 1365, 1345								
10/III	186	3394 b					1553, 1540, 1522	1372, 1350, 1338	498	535	638					

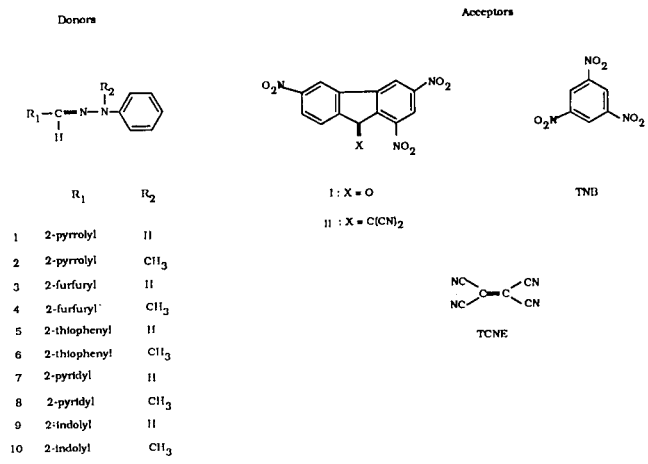
From te experimental data in solution, the following results are seen: (1) in almost all the cases, complexes of methylphenylhydrazones absorb at higher wavelengths with respect to the simple phenylhydrazones (a reverse behaviour is found in complexes of donors **7**, **8** with TNB, TNF and DTF); (2) the comparison of the λ max (chloroform) of complexes of benzaldehydemethylphenylhydrazone (514 nm) [13] and of methylphenylhydrazones **2**, **4**, **6**, **8** and **10** with TNB (Table 1) indicate that the contribution to the transition energy by the heterocyclic ring, in terms of transmission of electronic effects, is similar to the one induced by the phenyl ring; this fact allows us to hypothesize that π orbitals of the heterocyclic moiety, mainly, are involved in the MC transition [14]. Exceptions can be found in complexes of **2** and **10** where hydrogen bonding can be responsible for the higher λ max values.

The K_f values in complexes of methylphenylhydrazones **2**, **4** and **6** (where hydrogen bonding by the hydrazone group is forbidden) are related to the nature of the heteroatom, with the sulfur atom contributing more than nitrogen or oxygen (Table 1) [15]. In the complex **2**/TNB, either π-π^* interactions and hydrogen bonding contribute to the association while in systems **4**/TNB and **6**/TNB π-π^* interactions are operating mainly [a,15]. The K_f value quoted for the system **8**/TNB (0.24 ± 0.47 ℓmol^{-1}), can not be considered reliable (all attempts to optimize the experimental procedure were unsuccessful). A discrete contribute to the value of the formation constant comes from the hydrazone moiety (Table 1) [3]: as a matter of fact, K_f values of pyrrole/TNB (0.2 ℓmol^{-1}, chloroform) and thiophene/TNB (0.1 ℓmol^{-1}, chloroform) [16], appear much lower than those of complexes of hydrazones **2** and **6** with the same acceptor.

For sake of comparison, we also considered the value of the formation constant for the system benzene/TNB [17]. The value (0.82 ℓmol^{-1}, chloroform) appears unlikely if compared: (i) with the K_f of the complex benzaldehydemethylphenylhydrazone/TNB (0.77 ℓmol^{-1}, chloroform) [13]; (ii) with K_f values quoted in the systems benzene/TCNE (1.0 ℓmol^{-1}, carbon tetrachloride and 0.8 ℓmol^{-1}, dichloromethane) and thiophene/TCNE (1.04 or 1.0 ℓmol^{-1}, carbon tetrachloride and 0.84 ℓmol^{-1}, dichloromethane) and furan/TCNE (0.56 $\ell mole^{-1}$, carbon tetrachloride) [15,18].

In Figure 1 the plot of ν MC for complexes of TNF against ν MC for the corresponding complexes of DTF with donors **1-8** is reported. The linear correlation and the unit gradient in both cases can derive from the fact that the two acceptors involve in the complex the same orbitals [4,19-21]. Similar plots for complexes of acceptors TNF/TNB or DTF/TNB, even if linear, do not have an unit gradient. In the uv-visible spectra of solid complexes of TNF and DTF (Table 2), the main bands have the same features of those in solution, meaning that similar interactions are operating in the two phases. Even if the broadness of the bands do not allow detailed considerations, the red-shifts of the main bands in the solid state with respect to those in solution, can be a consequence of the crystallization [22,23]. The ranges of the shifts in the complexes of TNF, DTF and TNB are 100-150, 20-100 and 80 nm (**10**/TNB), respectively.

Scheme



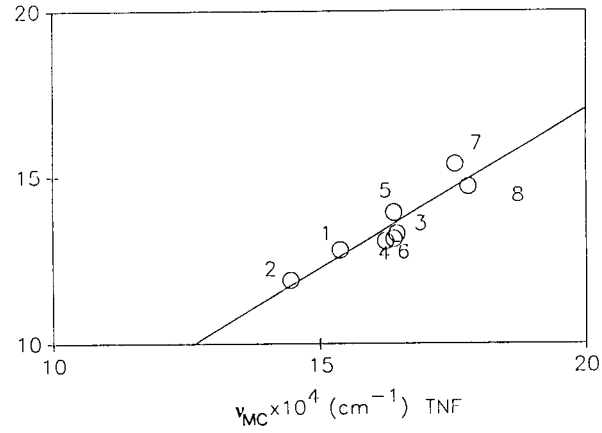


Figure 1. Plot of ν MC bands for complexes of TNF against ν MC bands for the corresponding complexes of DTF with donors 1-8 in chloroform solution.

Infrared Results.

The ν NH stretching modes of the hydrazone moiety in complexes of donors **1**, **7**, **9** and of donors **3**, **5** with TNF and DTF display apparent shifts to higher and to lower wave numbers, respectively; in the second group, an additional band can be found at *ca* 3245 cm^{-1}.

This behaviour can be related to the presence of two types of interactions: n-π^* interaction (from the amino nitrogen of the hydrazone rather than from the endocyclic

nitrogen atom, due to the higher basicity of the former with respect to the latter [24,25]) and hydrogen bonding (with ν NH of the donor to higher and to lower wave numbers, respectively [26]). In the first group of complexes both effects can operate and the absorptions are to be considered a compromise between the two effects.

The change in environment of the NH group of the heterocyclic ring in complexes of donors **1**, **7**, **9** and its involvement in hydrogen bonding with one NO_2 group of the acceptor, is evidenced by the red shift and by a marked broadening in profile [27-29].

The ν CN stretching modes, present in DTF as two bands at 2230 and 2222 cm^{-1}, in the complexes usually are resolved in a single band at slightly lower wave numbers with respect to the band at 2230 cm^{-1}.

The carbonyl band of TNF exhibits none or small shifts to lower wave numbers; in the latter case, the shift can be due to an higher polarization and an increased charge density on the CO group for the formation of π-π^* stacked complexes [30]. In these systems the formation of hydrogen bonded complexes by the carbonyl group has been excluded by the same authors [4,31]. The intensity of ν C=N bands of the donors is diminished or completely eliminated; in the former case the absorption frequency remains practically unaffected. Even if the literature discusses the difficulty in localization of this band (owing to the proximity of strong aromatic ν C=C bands) [32-34], this problem can be overcome by using a high-resolution spectrometer (Figure 2) [29] and bands splitting procedures (Figure 3a,b). The decrease of the ν C=N band intensity, indicative of some contribution to the association, support the hypothesis that the imino group can also participate as a donor in the association with planar acceptors [2,32-38].

The shifts to lower wave numbers or the decrease in band intensity in the stretching modes of CN, CO and C=N, are indicative of an unique trend caused by an enhancement of charge density and asymmetry in the molecule of the acceptors [39,40]

Three bands are detected for NO_2 asymmetrical in DTF and for NO_2 asymmetrical and NO_2 symmetrical in TNF, while only two bands are recorded for NO_2 symmetrical in DTF. In the complexes of TNF and DTF, small shifts to higher wave numbers are displayed by the NO_2 asymmetrical modes, with bands better resolved with respect to the acceptors alone and with the highest intensities corresponding to the lowest energy band. It is known that a shift to higher energies denotes the occurrence of an interaction involving a n-π^* transition or an hydrogen bonding and, by contrast, a shift to lower energies result from π-π^* transitions (as a consequence of an increased polarization of the nitro group in the complex). The overall values of NO_2 asymmetrical stretching modes allows one to suppose a prevailing occurrence of hydrogen bonding and n-π^* over π-π^* transitions (even if these are to be considered a compromise between the three types of interactions) [25,38].

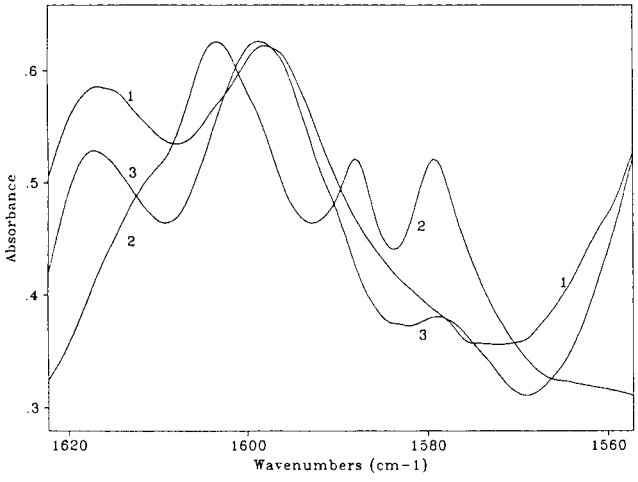


Figure 2. A view absorptions in the region 1620-1560 cm^{-1}: [1] TNF; [2] hydrazone 5; [3] system 5/TNF.

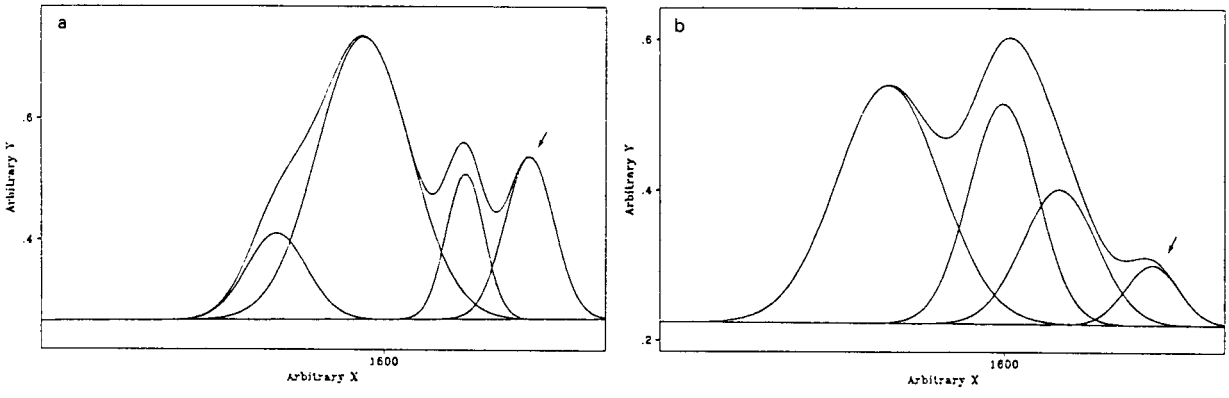


Figure 3a,b. Bands splitting the region 1620-1560 cm^{-1}: (a) hydrazone 5. (b) system 5/TNF. The arrow points out the ν C=N absorption.

Shifts to higher wave numbers are found in NO_2 symmetrical vibrations, too, except for the second band in complexes of DTF which falls at lower energies than the one of the free acceptor. In almost all the complexes, the NO_2 symmetrical modes of DTF (two bands) are resolved into three bands revealing a higher differentiation in the energies of the nitro groups in the complex [41].

As reported above, in the case of TNB, we were able to synthesize only the solid complex **10**/TNB. In this complex the ν NH band absorbs at lower wave numbers while no change in frequency is observed in ν C=N with respect to the starting hydrazone. In the complex, NO_2 asymmetrical and NO_2 symmetrical stretching modes of TNB fall at lower frequencies [42].

With respect to the components, the δ CH and the γ CH of the acceptors and of the donors shift in the complexes to lower and to higher wave numbers, respectively, as a consequence of some π-π^* contribute of the aromatic rings to the bonding in the complexes. The following shifts are registered in the complexes with respect to the acceptor: (a) δ CH of TNF (1086, 1069 cm^{-1}), 1-9 cm^{-1}; (b) δ CH of DTF (1105 cm^{-1}), 3-5 cm^{-1}; (c) γ CH of TNF (839-739 cm^{-1}), 1-15 cm^{-1}; (d) γ CH of DTF (830-730 cm^{-1}), 1-14 cm^{-1}; (e) δ CH of TNB (1088, 1077 cm^{-1}), 14-18 cm^{-1}; (f) γ CH of TNB (830, 827, 755 cm^{-1}), 9-12 cm^{-1}; (g) a group of bands, representing the δ CH (1130-1000 cm^{-1}) and the γ CH (850-730 cm^{-1}) modes of the donors, are shifted 1-6 cm^{-1} [41-44].

The band around 920 cm^{-1} (attributed to the C–N stretching vibration), in the complexes is found at lower wave numbers, with the following shift ranges: TNF (921 cm^{-1}), 2-8 cm^{-1}; DTF (910 cm^{-1}), 2-7 cm^{-1}; TNB (920 cm^{-1}) 4 cm^{-1} (**10**/TNB).

ESR Results.

We have reported in previous work that, in complexes of hydrazones with quinoid acceptors like chloranil, the formation of radical species allows one to hypothesize that the complex may be an intermediate in the mechanism of dehydrogenation of hydrazones [45]. In order to obtain evidence of the electron transfer in our systems, we tried to experiment in the presence of trichloroacetic acid or potassium *tert*-butylate, that increases the electron withdrawing or electron releasing character of the acceptor or of the donor, respectively. By dissolving our complexes in polar media, or by adding trichloroacetic acid as well as potassium *tert*-butylate to a solution of the complex in apolar solvents, weak and unresolved esr signals were detected. On the other side, no signal was detected in solutions of the donor or the acceptor alone with trichloroacetic acid or potassium *tert*-butylate, respectively. Even if the results do not allow any definite conclusion, they suggest that there should be some contribution from a dative structure to the energy of the complex in the ground state [46].

Acetonitrile solutions of complexes of TCNE always gave an esr spectrum of nine resolved lines attributable to the TCNE anion radical. This fact, however, can not constitute definite proof that the radical anion comes from the complex, due to the possibility to detect it from a solution of TCNE if rigorously anhydrous conditions are not used [47].

EXPERIMENTAL

The uv-visible measurements in solution were carried out on a Perkin Elmer 554 spectrophotometer equipped with a MgW-K2R thermostat system and the temperature was kept constant within $\pm 0.1°$. The uv-visible solid-state spectra were obtained on the same spectrophotometer equipped with a Perkin Elmer integrating sphere. The ft-ir measurements in the solid state were carried out on a Nicolet Fourier Transform Infrared 20-SX spectrometer, equipped with a Spectra Tech. Multiple Internal Reflectance "Collector". Band splittings were performed using a Galactic package software, supposing a Gaussian character. Melting points were determined on a micro hot-stage apparatus and are uncorrected. Mass spectra were obtained with a Carlo Erba Model QMD 1000 mass spectrometer. The esr spectra were recorded on a Varian E-4 spectrometer using a deaerated two-leg inverted cell described previously [48]. Hydrazones **1-10** were synthesized following the literature [1,49]. All solvents were Fluka spectroscopic grade and purified according to the literature [50].

General Procedure for the Synthesis of Solid Complexes of Donors **1-10**.

Almost saturated acetonitrile solutions of the reagents were mixed together at room temperature, the coloured precipitates were filtered off. Melting points and elemental analysis are reported in Table 1.

General Procedure for the Synthesis of Complexes of Donors **1-10** in Solution.

Equimolar solutions of donor and acceptor in the solvents reported in Table 1, were mixed at room temperature with stirring and the λ max of the MC bands were measured.

Formation Constants Determinations.

The formation constants were measured spectrophometrically in chloroform solution at 20°. According to the Benesi-Hildebrand method [51], the concentration dependence of the absorbance of the charge-transfer band (d) for a 1:1 complex is given by:

$$[A]_o/d = 1/K_f\epsilon[D]_o + 1/\epsilon$$

under conditions in which the total concentration of the electron donor $[D]_o$ is in large excess with respect to the total concentration of the acceptor $[A]_o$ and for a 1 cm light path. The K_f is the formation constant and ϵ is the molar extinction coefficient of the complex at the monitoring wavelength. Plots of $[A]_o/d$ against $1/[D]_o$ for solutions in which $[D]_o >> [A]_o$ should be linear.

For the calculation of the formation constants, the experimental data were computed by using a program from Dr. J. A. Chudeck, University of Dundee (Scotland), whom we ac-

knowledge.

As a general procedure, we report the uv-visible spectrophotometric measurements on the complex **6**/TNB in chloroform at 20°.

Twenty samples of donor **6** were weighed out to have a range of concentrations from 0.04 to 0.24 *M*. To each sample, 1 ml of TNB solution (9.41 mmoles) was added. The final volume was 3 ml. An average of the absorbance from three different determinations was taken. A linear correlation was obtained by plotting $[A]_o/d$ against $1/[D]_o$ and the correlation coefficient was greater than 0.999. The presence of termolecular species (D_2A) was excluded in the light of the Scatchard method.

ESR Determinations.

The reagent solutions were poured in each of the two legs of an inverted U cell and degased by nitrogen [48]; then, the solutions were mixed into an aqueous cell which was then transferred into the esr cavity. In other experiments, trichloroacetic acid or potassium *tert*-butylate were introduced in one leg of the cell and the reagents solution in the other one, working as described above.

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* To whom correspondence should be addressed.

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