The 90 wt % nitric acid with the urea was added slowly with cooling to an equal amount of purified 70 wt % nitric acid to give 80 wt % nitric acid as required for the reaction. All reactions were performed under an inert atmosphere. The 1000 mL of 80 wt % white fuming nitric acid was then cooled to −10 °C. Urea (20 g) was slowly added to the reaction mixture as a nitrous acid trap. Next, 161 g (0.82 mol) of resorcinol diacetate was slowly added with stirring at a rate sufficient to maintain a temperature at or below 5 °C. Extreme caution must be used at this stage of the reaction, because adding the resorcinol diacetate too rapidly or allowing the temperature to rise above 0 °C can lead to a fume off. A yellowish-gold precipitate will slowly form in the nitric acid/urea solution. After approximately 2 h, the precipitate was collected by filtration with use of a glass filter paper. The remaining nitric acid solution was poured onto ice and filtered again to remove any additional precipitate. The precipitate was washed several times with water, dried, and recrystallized from ethyl acetate. The isolated yield of recrystallized material from the reaction was 56.4 g (44%). We can also isolate 4-nitroresorcinol and 2,4,6-trinitroresorcinol (styphnic acid) from the water/nitric acid mixture. Mass spectrum of 4,6-DNR: m/e 200 (M^+), 184 (M − O), and m/e 170 (M − NO).

Synthesis in Nitric Acid/Sulfuric Acid. *CAUTION*: This synthesis has inherent dangers. While in practice we have found this method to be considerably safer and more reliable than the corresponding nitric acid method above, this reaction involves solutions of sulfuric acid, nitric acid, and resorcinol diacetate, which have been known to react violently after an induction period (fume off)!! 2,4,6-Trinitroresorcinol (styphnic acid—*CAUTION*—explosive!!) is formed as a byproduct in this reaction.

As described above, 80 wt % nitric acid is purified to eliminate all NO_2, N_2O_4, or nitrous acid. Three molar equivalents (relative to the resorcinol diacetate) of purified nitric acid (46.5 g) was then added slowly to 1000 mL of 80 wt % H_2SO_4, which was cooled to −10 °C. Small amounts of urea were added to control any nitrous acid formed in the reaction. Resorcinol diacetate (47.53 g) was slowly added with stirring, while the reaction temperature was kept below 0 °C. A yellowish-gold precipitate slowly formed, and the reaction was worked up as described above after 1.5 h. The isolated yield of recrystallized 4,6-DNR was 60%.

Acknowledgment. We thank Dr. Robert C. Evers of AFWAL (Contract No. F33615-84-C-5005) for his encouragement and support of this work.

Evidence of Termolecular Complex Formation of Tetrabromo-*p*-benzoquinone with Certain Nonaromatic Donors

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Received June 7, 1988

In recent spectrophotometric studies of the interaction of *p*-chloranil and *p*-fluoranil as electron acceptors (Ac) with various electron donors (D), including ethers, amides, lactones, and related compounds, evidence has been obtained in some cases that 2:1 (D_2Ac) as well as 1:1 (DAc) complexes are formed.[1,2] Presumably in the termolecular complex the two donor molecules coordinate on opposite sides of the acceptor ring. Termolecular complex formation becomes more apparent as the donor strength increases and also is observed more frequently with *p*-fluoranil than with *p*-chloranil as the acceptor, no doubt in reflection of the relative acceptor strengths[3] of the two tetrahalobenzoquinones.

These earlier investigations of *p*-chloranil and *p*-fluoranil complexes have now been extended to determine the disposition of *p*-bromanil to undergo complex formation with a number of the same electron donors used previously. Since *p*-bromanil has been reported to be the weakest of the three *p*-tetrahaloanils,[3] it has seemed of interest to determine whether any detectable evidence that it engages in termolecular complex formation can be obtained.

Experimental Section

Materials. The sources of the donors and of the carbon tetrachloride used as solvent were the same as described previously.[1,2] The *p*-bromanil was obtained from Lancaster Synthesis.

Determination of Equilibrium Constants. For each donor investigated a series of carbon tetrachloride solutions of varying concentration of the donor and fixed concentration of *p*-bromanil (usually of the order of (7–8) × 10^{-4} M) were prepared at 25.0 °C. Generally eight to ten such solutions were used, the donor concentrations of which varied over more than a 10-fold range. To improve the chances of obtaining evidence of termolecular complex formation, the most concentrated solutions were of the order of 5–7 M, except in the cases of lactam donors (2–3 M). The spectrophotometric equipment that was used and the general method of determining the absorbances of these solutions at various wavelengths were the same as described previously.[1] In most instances the absorbance of each solution was measured at several wavelengths in the 390–310-nm range, at which the complexes absorb appreciably more than the free acceptor. Solutions containing lactones and triethyl orthoformate were also measured in the 330–260-nm range at a *p*-bromanil concentration level of 7 × 10^{-5} M.

In a few instances equilibrium constants for formation of *p*-fluoranil complexes of the donor used in the *p*-bromanil studies had not been previously determined. These were obtained for comparison purposes by essentially the same procedures as used in the earlier work on *p*-fluoranil complexes.[2]

The experimental data obtained at a particular wavelength for the series of solutions of varying donor concentration were treated graphically by the Ketelaar equation (1)[4] on the assumption that only a 1:1 complex with an equilibrium constant of K_c is formed (eq 2). In eq 1, $\epsilon_a = A/l[Ac]_t$ where A is the absorbance of the

$$\frac{1}{\epsilon_a - \epsilon_{Ac}} = \frac{1}{\epsilon_c - \epsilon_{Ac}}\left(\frac{1}{K_c[D]}\right) + \frac{1}{\epsilon_c - \epsilon_{Ac}} \quad (1)$$

$$K_c = [DAc]/[D][Ac] \quad (2)$$

solution of donor and acceptor, l is the light path length in centimeters, and $[Ac]_t$ is the total concentration of acceptor (free and complexed) in moles/liter; ϵ_{Ac} and ϵ_c are the molar absorptivities of free and complexed acceptor, respectively. The donor concentration, [D], was expressed in moles/liter. In those cases in which plots of $1/(\epsilon_a - \epsilon_{Ac})$ values at a particular wavelength vs corresponding 1/[D] values were linear over the entire donor concentration range, K_c values were calculated from the slopes and intercepts. In those cases in which the lines curved downward at higher donor concentrations, later reported K_c values were based on linear portions of the plots. In such cases, as has been discussed in detail recently,[1,2] a procedure based on the discussion of Deranleau[5] was applied in estimating K_1 and K_2 values (eq 3).

$$K_2 = [D_2Ac]/[D][DAc] \quad (3)$$

The K_1 values so obtained are K_c values that have been corrected in recognition of the formation of termolecular as well as bimolecular complexes. Less likely interpretations of the data are dealt with in the earlier publications.[1,2]

Results and Discussion

The K_c values for interaction of the various electron donors with *p*-bromanil are summarized in Table I. The corresponding values of K_c for the *p*-chloranil and *p*-

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0022-3263/88/1953-5569$01.50/0

Table I. K_c Values for the Tetrahalo-*p*-benzoquinone Complexes (CCl_4 Solvent, 25.0 °C)[a]

donor	K_c, L mol^{-1} bromanil acceptor	chloranil acceptor	fluoranil acceptor
triethyl orthoformate	small?	0.84 ± 0.02[b]	3.1 ± 0.2[b]
ϵ-caprolactone	small?	1.08 ± 0.1[c]	4.8 ± 0.3[c]
γ-butyrolactone	small?	0.34 ± 0.03[c]	2.24 ± 0.15
cyclohexanone	0.67 ± 0.04	0.86 ± 0.09[c]	1.7 ± 0.2[c]
2,5-hexanedione	0.54 ± 0.04	1.47 ± 0.07[c]	ca. 2.[d]
2,4-pentanedione	0.26 ± 0.02	0.33 ± 0.02[c]	ca. 0.9[d]
tetrahydrofuran	0.51 ± 0.03	0.54 ± 0.02[e]	0.81 ± 0.02[b]
1,4-dioxane	0.48 ± 0.02	0.40 ± 0.05[f]	0.56 ± 0.05[b]
N,N-diethylacetamide	2.2 ± 0.09	2.4 ± 0.3[c]	7.2 ± 0.3[c]
N,N-dimethylacetamide	1.31 ± 0.15	2.4 ± 0.3[c]	6.6 ± 0.35
N-methylacetamide	0.55 ± 0.02	0.80 ± 0.08[c]	2.8 ± 0.2
N,N-dimethylformamide	0.83 ± 0.05	1.7 ± 0.2[c]	2.5 ± 0.07
δ-valerolactam	2.6 ± 0.3	3.5 ± 0.3	7.5 ± 0.4
ϵ-caprolactam	1.13 ± 0.06	2.6 ± 0.5[c]	6.4 ± 0.5[c]

[a] Reported values of K_c are averages of values obtained through measurements at several wavelengths. [b] From ref 1. [c] From ref 2. [d] The scatter of points in the Ketelaar plots of the data was such that the K_c value can be reported only approximately. [e] This value is based on measurements at a larger number of donor concentrations than were used in determining the value reported previously[1] (0.40 ± 0.05 L mol^{-1} for tetrahydrofuran and 0.25 ± 0.03 L mol^{-1} for 1,4-dioxane).

fluoranil complexes are also listed for comparison purposes. Some of the values listed for the *p*-fluoranil complexes were obtained in the present study (those for which no reference to previous work is given). In several instances the K_c values for particular donors diminished as the electron acceptor was changed in the order fluoranil–chloranil–bromanil. In most cases the K_c values were somewhat more influenced by changing the acceptor from fluoranil to chloranil than from chloranil to bromanil. The K_c values for the complexes of the relatively weak donors, among them tetrahydrofuran and 1,4-dioxane, were relatively insensitive to the changes in acceptor. In their interactions with all three of the tetrahalobenzoquinones, the lactams and amides proved to be the strongest of the donors included in this investigation.

Attempts to obtain reliable K_c values for the interaction of *p*-bromanil with triethyl orthoformate, ϵ-caprolactone and γ-butyrolactone proved futile. Unlike what is observed when *p*-chloranil or *p*-fluoranil is the acceptor,[2] the absorption spectrum of *p*-bromoanil in carbon tetrachloride solutions of these three donors is not substantially different from that of that acceptor in pure carbon tetrachloride at any wavelength in the 260–400-nm range. This is illustrated specifically for the system, γ-butyrolactone–*p*-bromanil in Figure 1, which covers only the 280–400-nm range. Curves 1 and 2 of this figure represent the spectrum of *p*-fluoranil in carbon tetrachloride and in a γ-butyrolactone–carbon tetrachloride solution, respectively. In the region of 280–300 nm, absorption in the presence of the donor is significantly greater than in the absence of the lactone, sufficiently so that K_c values can readily be calculated from data recorded in this region. Curves 3 and 4 of the figure apply to solutions of *p*-bromanil in carbon tetrachloride and in a γ-butyrolactone–carbon tetrachloride solution. In the 330–400-nm region the spectra are closely similar and, in fact, unlike the spectra of the corresponding *p*-fluoranil containing solutions, remain so down to 260 nm. Both of the bromanil-containing solutions display major absorption maxima, close to each other in intensity, at 310 nm. They display minima at 270 nm, at which the lactone-containing solution absorbs somewhat more intensely than the lactone-free solution. The differences are not sufficiently great to be useful in calculating

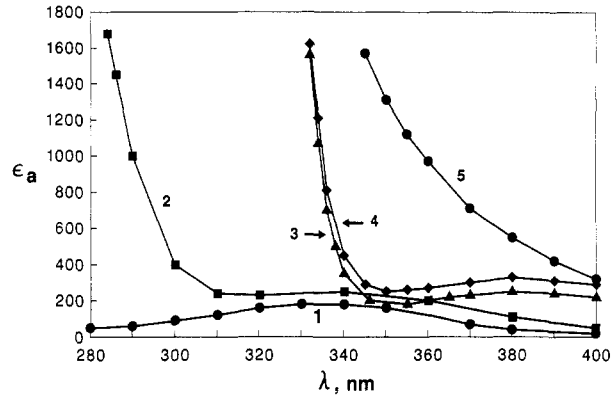
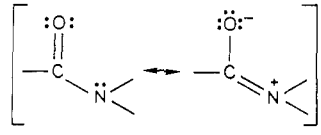


Figure 1. The spectra of *p*-fluoranil in a carbon tetrachloride solution of γ-butyrolactone and of *p*-bromanil in carbon tetrachloride solutions of γ-butyrolactone and *p*-dioxane (25.0 °C). Curve 1, *p*-fluoranil in CCl_4; curve 2, *p*-fluoranil in 6.61 M γ-butyrolactone; curve 3, *p*-bromanil in CCl_4; curve 4, *p*-bromanil in 6.607 M γ-butyrolactone; curve 5, *p*-bromanil in 5.305 M *p*-dioxane.

equilibrium constants. Spectral behavior closely similar to that of bromanil–γ-butyralactone is observed for bromanil–ϵ-caprolactone and bromanil–triethyl orthoformate. By contrast the absorption of *p*-bromanil in the presence of other donors investigated is sufficiently different from that in donor-free solution to permit evaluation of K_c values (see, for example, curve 5, Figure 1, for *p*-bromoanil–1,4-dioxane).[6]

It must be concluded either that K_c values for interaction of *p*-bromanil with the lactones and the orthoformate are very small or that the complexes that are formed have spectra that are very similar to that of the bromanil throughout the region in which measurements were made. The latter alternative seems unlikely since it is not the case for any other donor–*p*-tetrahalobenzene complex that has been investigated. If, indeed, the K_c values for the three bromanil complexes in question are unusually small, the explanation might lie in the simultaneous involvement of two oxygen atoms of the donor molecule (or perhaps all three oxygens in triethyl orthoformate) in coordination with a bromanil molecule. Those oxygen atoms presumably would lie close to the ring perimeter of the acceptor molecule. Because of the combined bulk of the four bromine atoms on the acceptor ring, the close approach of the donor oxygens to the ring perimeter required for effective interaction might be impeded. A steric problem of this nature should not be nearly so major with *p*-chloranil, and less so with *p*-fluoranil, as the acceptor. The explanation for the fact that there is no obvious steric barrier to interaction of amides and lactams with *p*-bromanil may lie in the relatively high degree of resonance stabilization in such donors molecules.[7] The coordination center of donors of this kind may be the oxygen atom (rather than both oxygen and nitrogen simultaneously).



(6) Except as noted the spectra of *p*-bromanil–donor solutions are shaped like those of the corresponding *p*-fluoranil– and *p*-chloranil–donor solutions[2,3] but increasingly displaced toward the visible region as the acceptor is changed from fluoranil to bromanil.

(7) For pertinent discussion, see for example: (a) Connors, K. A. *Reaction Mechanisms in Organic Chemistry*; Wiley-Interscience: New York, 1973; pp 564–565. (b) Wade, L. G., Jr. *Organic Chemistry*; Prentice-Hall: Engelwood Cliffs, NJ, 1987; pp 1020–1021.

Table II. Values of K_1 and K_2 for Certain of the Complexes (CCl_4 Solvent, 25.0 °C)

donor	K_1, L mol^{-1}	K_2 L mol^{-1}
p-Bromanil Complexes		
cyclohexanone	1.01 ± 0.06	0.141 ± 0.006
tetrahydrofuran	0.75 ± 0.04	0.095 ± 0.004
N,N-diethylacetamide	2.89 ± 0.09	0.314 ± 0.010
N,N-dimethylacetamide	1.73 ± 0.17	0.19 ± 0.01
N-methylacetamide	0.87 ± 0.06	0.132 ± 0.012
N,N-dimethylformamide	1.06 ± 0.08	0.096 ± 0.008
δ-valerolactam	4.2 ± 0.05	0.63 ± 0.08
p-Fluoranil Complexes		
γ-butyrolactone	2.99 ± 0.15	0.31 ± 0.03
N,N-dimethylacetamide	7.67 ± 0.36	0.61 ± 0.04
N-methylacetamide	3.56 ± 0.21	0.44 ± 0.04
N,N-dimethylformamide	2.97 ± 0.04	0.21 ± 0.01
δ-valerolactam	8.54 ± 0.38	0.65 ± 0.05

Table II provides a summary of K_1 and K_2 values for *p*-bromanil complexes of certain of the donors for which K_c values are listed in Table I. These were evaluated from those Ketelaar plots of spectral data, which showed significant deviations from linearity in the region of high donor concentration. Table II also gives a summary of K_1 and K_2 values for certain *p*-fluoranil complexes that were not reported previously. In general, the relatively strong donors, the amides and lactams, provide readily apparent evidence of termolecular as well as bimolecular complex formation with *p*-bromanil. Cyclohexanone and tetrahydrofuran are included with those donors for which evidence of termolecular complex formation with this acceptor has been obtained. At first glance it may seem surprising that *p*-bromanil is as favorably disposed to undergo termolecular complex formation as it is. Actually a number of donors interact about as well with *p*-bromanil as with *p*-chloranil (see Table I). This is in keeping with the fact that the halogen atoms, bromine and chlorine, are not far apart in electronegativity, though they are substantially less electronegative than the fluorine atom.[8] Aside from possible steric problems, as discussed above, the differences in electronegatives of the halogens should be directly reflected to a considerable degree in the relative strengths of the three tetrahlobenzoquinones as acceptors.

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Deoxygenation of Sulfoxides Promoted by Electrophilic Silicon Reagents: Preparation of Aryl-Substituted Sulfonium Salts

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Received May 17, 1988

The utility of substituted sulfonium salts in organic chemistry is manifested by the development of numerous synthetic routes to these materials.[1] Simple unhindered alkyl sulfonium salts are normally prepared by the direct alkylation of the corresponding sulfides by a wide variety of common alkylating reagents. Unfortunately, this technique is less successful for the preparation of sterically hindered or polyaryl-substituted materials.[1d] The preparation of sulfonium salts of this type usually requires the use of metallic complexing reagents[2] and/or the use of powerful electrophilic reagents.[3] The latter is epitomized by the sulfide arylation reaction, which requires the use of very electrophilic species such as aryl diazonium ions[4] or iodonium salts.[5] Recently, Julia and co-workers have reported the synthesis of a number of diphenyl alkyl substituted sulfonium salts by the alkylation of diphenyl sulfide with the corresponding alcohols in the presence of a variety of strong acids employed in excess.[6]

The recent discovery that triaryl-substituted sulfonium salts (Ar_3SMX_n) constitute a new class of thermally stable, nontoxic materials that produce protic acids upon irradiation has greatly stimulated interest in compounds of this type.[7] Synthetically, the direct addition of organometallic reagents to the corresponding diaryl sulfoxides followed by acidic hydrolysis constitutes perhaps the simplest and most straightforward route to triaryl sulfonium derivatives. In principle, this reaction was demonstrated by Wildi and co-workers,[8] although the procedure as described lacks generality, employs harsh reaction conditions that require large excesses of the organometallic reagents, and even under the best circumstances produces the desired sulfonium salts in mediocre yields. In addition, we have also recently discovered that it is unsuitable for the preparation of a number of unsymmetrical derivatives due to rapid ligand exchange under the reaction conditions.[9] The ligand exchange is exacerbated by the need for elevated temperatures and large excesses of Grignard reagent.

An alternative synthetic route has recently been reported by Crivello and Lam[10] which employs the thermal, copper-catalyzed, decomposition of aryl-substituted iodonium salts containing certain nonnucleophilic counterions in the presence of diphenyl sulfide.[10] This procedure, however, is multistep, requires the preparation and isolation of toxic iodonium salts, and fails in the presence of nucleophilic counterions.

The ready availability of sulfoxide starting materials makes the direct addition of organometallic reagents particularly attractive, provided the earlier difficulties can be overcome. For this, sulfoxide activation is essential to permit the addition to occur rapidly under mild reaction conditions, preferably with stoichiometric quantities of the organometallic reagents. In this regard, it has recently been demonstrated[11] that certain electrophilic silicon

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