

RADICAL IONS IN THE REACTIONS OF *p*-CHLORANIL WITH TRIPHENYLPHOSPHINE AND WITH TRIETHYL PHOSPHITE

ELECTRON SPIN RESONANCE AND ULTRAVIOLET ABSORPTION SPECTRA

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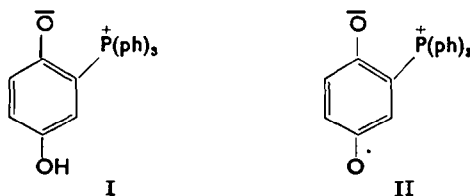
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Abstract—The colour and the ESR spectrum which develop during the reaction of triphenylphosphine with *p*-chloranil are due to a phenoxy-O-phosphonium radical cation and to a semiquinone radical anion. These are formed by oxidation of the phosphine, or of a phosphine-quinone complex, by quinone. The radical ions are not formed by oxidation of the final product of the reaction (a phenoxy-O-phosphonium dipolar ion) by *p*-chloranil *in solution*. The reaction of triethyl phosphite with *p*-chloranil produces analogous coloured species with unpaired electrons. The g-factors and the hyperfine constants (ΔH) for the radical cations from triphenylphosphine and triethyl phosphite, are, respectively: 2.0050, 2.42 gauss and 2.0051, 1.83 gauss.

INTRODUCTION

THE phosphorus of triphenylphosphine attacks a carbon of *p*-benzoquinone and forms an *ylide* or *phosphobetaine*^{4,5} (I). This ylide is oxidized by an excess of quinone giving a free-radical phosphobetaine (II) which was characterized by its electron spin resonance (ESR) spectrum.⁶



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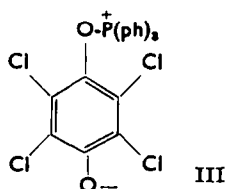
³ DuPont Postgraduate Teaching Assistant and U.S. Rubber Fellow at Columbia University. From part of the Ph.D. thesis of D.R. (Columbia University).

⁴ F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.* **78**, 5614 (1956).

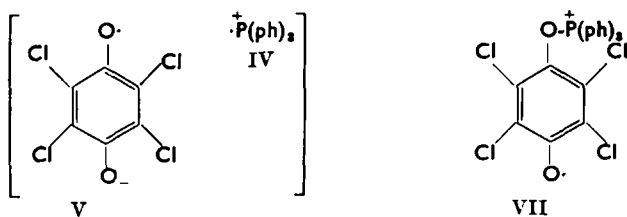
⁵ A previous formulation of this adduct by L. Horner and K. Klupfel, *Liebigs Ann.* **591**, 76 (1955) was later revised to the phosphobetaine structure by H. Hoffman, L. Horner and G. Hassel, *Chem. Ber.* **91**, 58 (1958).

⁶ E. A. C. Lucken, *J. Chem. Soc.* 5123 (1963).

The reaction of triphenylphosphine with *p*-chloranil takes a different course.⁴ When equimolar amounts of the reagents were mixed in benzene solution, in a dry nitrogen atmosphere, a red colour developed in the solution, accompanied by the slow and quantitative formation of a buff-coloured precipitate. Water instantaneously converted this precipitate into equimolar amounts of triphenylphosphine oxide and tetrachlorohydroquinone. Structure III, with a phosphorus-oxygen bond, accounts for the properties of this adduct. A dimer of III has not been ruled out.⁴



The red benzene solution resulting from the interaction of the phosphine and the quinone had an ESR spectrum consisting of two lines of equal intensity, with a separation of about two gauss. It was initially suggested⁷ that the chloranil oxidized one molecule of triphenylphosphine, directly or *via* a charge transfer complex^{8,9} forming a *phosphinium radical-ion*, (IV) and a chloranil semiquinone, (V) which by recombination could yield the product III. Another possibility^{4,7} was the oxidation of a second phosphine molecule by the semiquinone (V) with formation of more radical ion (IV) plus tetrachlorohydroquinone dianion (VI). Addition of the phosphinium radical ion (IV) to chloranil would yield a *phenoxy-O-phosphonium radical cation*, (VII). Reaction of VII with a second phosphinium radical (IV) could generate a bisphosphonium cation, which together with tetrachlorohydroquinone dianion (VI) would constitute the 2:2 adduct or dimeric alternative to the 1:1 adduct III.



Clearly, the species responsible for the electronic paramagnetism could not be exclusively the chloranil semiquinone (V) since this was known^{10,11} to give a one-line ESR signal. Furthermore, it soon became evident that the phosphinium radical ion, (IV) could not be involved, since an unpaired 3s-electron on a ³¹P nucleus should give rise to a large hyperfine splitting constant (ca. 3,300 gauss). The *phenoxy radical*

⁷ F. Ramirez and S. Dershowitz, *J. Org. Chem.* **22**, 856 (1957).

⁸ R. S. Mulliken, *Rec. Trav. Chim.* **75**, 845 (1956).

^{9a} H. Kainer, D. Bijl and A. C. Rose-Ines, *J. Chem. Phys.* **30**, 765 (1959); ^b *Naturwiss.* **41**, 303 (1954);

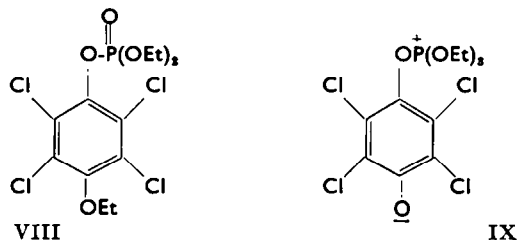
^c H. Kainer and A. Uberle, *Chem. Ber.* **88**, 1147 (1955).

^{10a} J. E. Wertz and J. L. Vivo, *J. Chem. Phys.* **23**, 2441 (1955); ^b W. Schlenk, *Liebigs Ann.* **368**, 281 (1909).

^{11a} B. Venkataraman and G. E. Fraenkel, *J. Amer. Chem. Soc.* **77**, 2707 (1955); ^b J. H. Baxendale and R. Hardy, *Trans. Faraday Soc.* **49**, 1433 (1953); ^c J. Gendell, J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962); ^d J. H. Freed and G. K. Fraenkel, *Ibid.* **40**, 1815 (1964).

cation (VII) remained as a possibility and further studies were undertaken. This paper describes the results.

Another reaction of chloranil, which gave colours and a two-line ESR signal, was that with triethyl phosphite.^{7,12} The product, now, was a stable ether of a *p*-quinol phosphate, (VIII) formed presumably from the transient dipolar ion (IX).



This reaction was also studied further, and the results are included in this paper.

RESULTS

UV absorption spectrum of the chloranil-triphenylphosphine system. The simplest type of interaction between chloranil and the phosphine was observed when solutions of the reagents in methylene chloride–isopropyl chloride were mixed at 20° and immediately cooled to 77°K. The glass which resulted had a red-violet colour; the spectrum of this glass is reproduced in Fig. 1, which shows maximum absorption at 515–520 $m\mu$. When the phosphine was omitted, the glass was pale yellow, which is the colour of chloranil.

No appreciable interaction between chloranil and the phosphine was observed when $5.0 \times 10^{-3}M$ solutions of the reagents in methylene chloride–isopropyl chloride were precooled to -70° and then mixed at -80° ; (Fig. 2, dotted curve 1). No changes were observed until a temperature of about -30° was attained (dashed curve 2); then, weak absorption maxima appeared at 385, 412 and 540 $m\mu$. This spectrum was better developed in solid curve 3 taken at -25° .

Figures 1 and 2 suggest: (a) that chloranil and triphenylphosphine can interact very rapidly to give only one species which absorbs beyond 520 $m\mu$; and (b) that other species, with absorption maxima at 388 and 412 $m\mu$ make their appearance with only slightly greater difficulty.

The spectral changes which occurred when methylene chloride solutions of the reagents were mixed at 25° are shown in Fig. 3. The spectra were begun 15 sec (dashed curve 1), 360 sec (solid curve 2) and 660 sec (dotted curve 3) after admixture. The scanning time was 4 min in each case. Absorption maxima at 388, 414 and 536 $m\mu$ appeared immediately and then decreased in intensity. The initial red-violet colour faded to light yellow as the maxima decayed. Absorption at, or below, 335 $m\mu$ is to be expected for the dipolar ion product (III) and for the dianion of tetrachloro-hydroquinone. The peaks at 388, 412 and 536 $m\mu$ decayed independently of each other. There was no absorption at 452 $m\mu$, corresponding to the maximum absorption of chloranil semiquinone⁹ (V).

^{12a} F. Ramirez and S. Dershowitz, *J. Org. Chem.* **23**, 778 (1958); ^b F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.* **81**, 587. (1959); ^c F. Ramirez, E. H. Chen and S. Dershowitz, *J. Amer. Chem. Soc.* **81**, 4338 (1959).

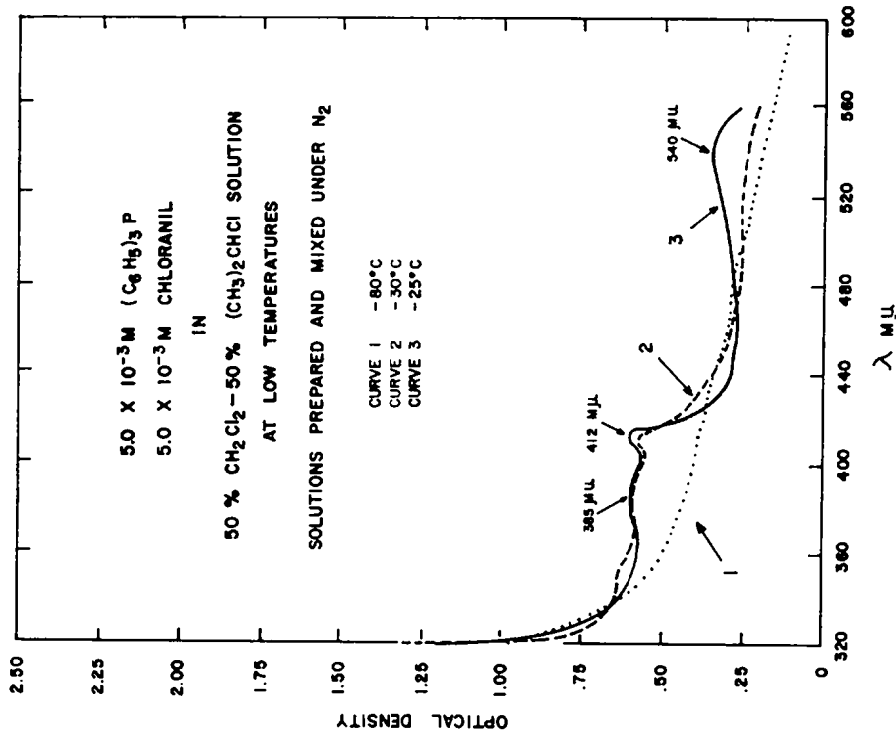


Fig. 2 UV spectrum of the solution obtained when $5.0 \times 10^{-3} \text{ M}$ solutions of chloranil and of triphenylphosphine in $50\% \text{ CH}_2\text{Cl}_2 - 50\% (\text{CH}_3)_2\text{CHCl}$ were mixed under N_2 at -70° . Curve 1, ..., taken at -80° ; Curve 2, ---, taken at -30° ; Curve 3, —, taken at -25° . Absorption at 388, 412 and 540 m μ began at ca. -30° .

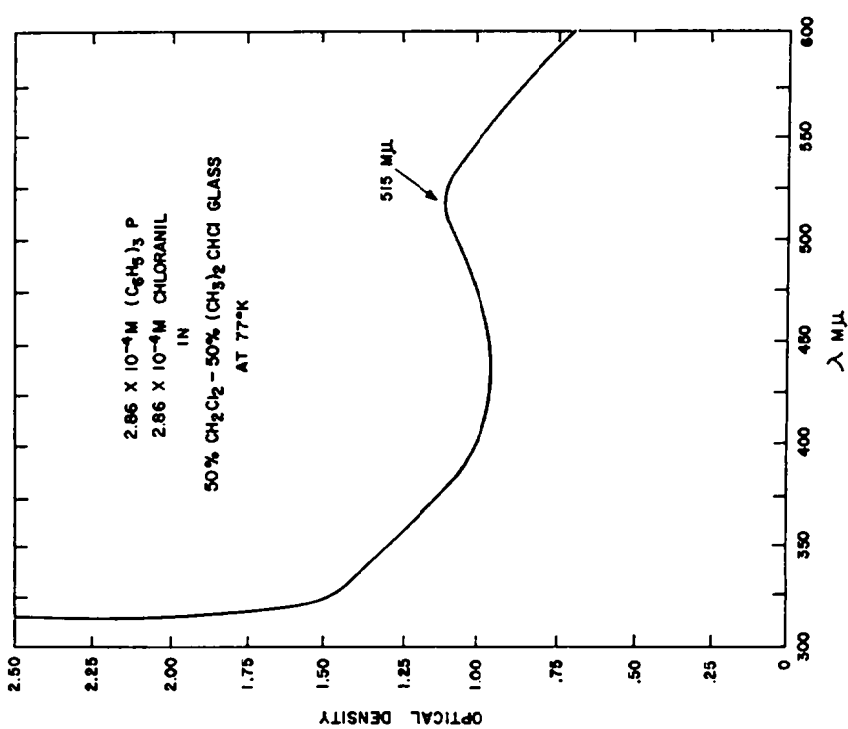


Fig. 1 UV Spectrum at 77°K of the red-violet glass obtained when $2.86 \times 10^{-4} \text{ M}$ solutions of chloranil and of triphenylphosphine in $50\% \text{ CH}_2\text{Cl}_2 - 50\% (\text{CH}_3)_2\text{CHCl}$ were mixed at 20° and immediately cooled to 77°K . λ_{max} at 515–520 m μ .

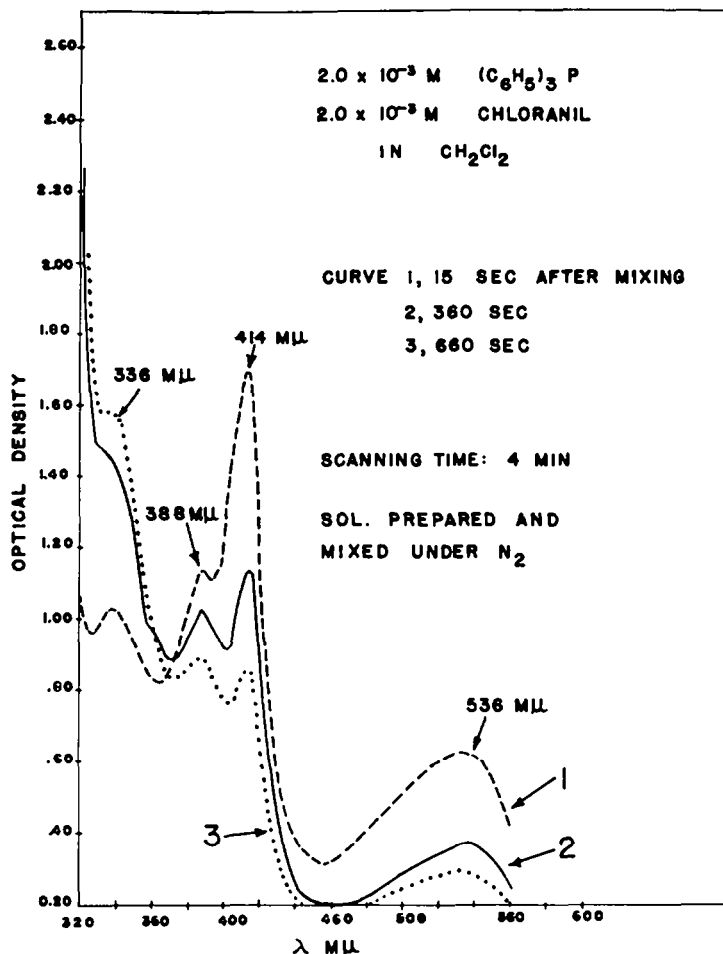


FIG. 3. Solutions of 2.0×10^{-3} M each of Chloranil and of triphenylphosphine were mixed in CH_2Cl_2 under N_2 at 25° ; Air excluded. Curve 1, ---, after 15 sec. Curve 2, —, after 360 sec. Curve 3, . . ., after 660 sec. Scanning time: 4 min for each curve.

Similar experiments, using more concentrated solutions (2.5×10^{-3} M) gave analogous results, except that the 388, 412 and 538 $\text{m}\mu$ maxima had higher intensities after 600 sec than after 100 sec. The intensities had decreased after 1800 sec, but there was still some absorption after 1 hr.

The spectra of solutions which were prepared and mixed in air showed significant differences. These solutions were bright orange instead of red-violet and showed the presence of chloranil semiquinone at $452 \text{ m}\mu$ (Fig. 4). For comparison, an aired, alkaline, methanolic solution of tetrachlorohydroquinone showed maxima at 425 and $452 \text{ m}\mu$ due to semiquinone, and a maximum at $330 \text{ m}\mu$ due to the dianion.

Note that in Fig. 4, the $412 \text{ m}\mu$ peak is always more intense than the $388 \text{ m}\mu$ band; i.e., the $412 \text{ m}\mu$ peak is probably due to a product of partial oxidation. The $412 \text{ m}\mu$ peak was relatively strong even after 3 hr.

ESR spectrum of the chloranil-triphenylphosphine system. The red-violet solution

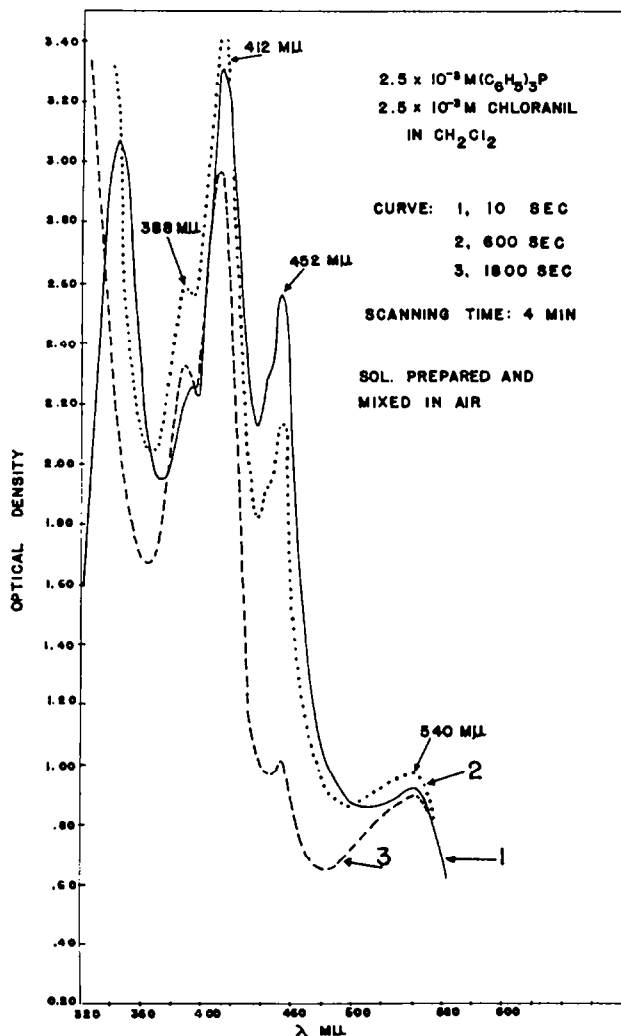


FIG. 4. Solutions of 2.5×10^{-3} M each of Chloranil and of triphenylphosphine were prepared and mixed in *air* in CH_2Cl_2 . Curve 1, —, after 10 sec. Curve 2, . . ., after 600 sec. Curve 3, ---, after 1800 sec. The maximum at 452 μ is due to chloranil semiquinone. Scanning time: 4 min for all curves.

obtained when the reagents were combined in benzene showed two peaks of equal intensities, with a g -factor = 2.0052 ± 0.0002 and a hyperfine splitting constant $\Delta H = 2.42 \pm 0.05$ gauss.

The same spectrum was obtained when the reagents were mixed in CH_2Cl_2 (Fig. 5). The ESR spectrometer was immediately turned to the reaction vessel and peak-heights were noted on the oscilloscope at various time intervals. The results are shown in Fig. 6.

When the solvent was scrupulously dry and free from alcohol, and when air was excluded, the two components of the ESR-doublet were of equal intensity. This

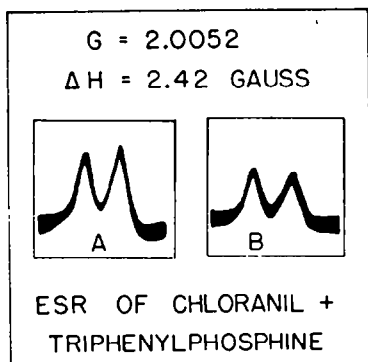


FIG. 5. Photographs of oscilloscope trace in the ESR spectrum of the chloranil-triphenylphosphine systems in CH_2Cl_2 , 7.12×10^{-3} M in each. (A) Taken 29 min after mixing. (B) Taken 94 min after mixing. Peak heights (at constant amplifier gain setting) in arbitrary units: (A) 5.7; (B) 3.2. Photographs were of long exposure time relative to sweep time.

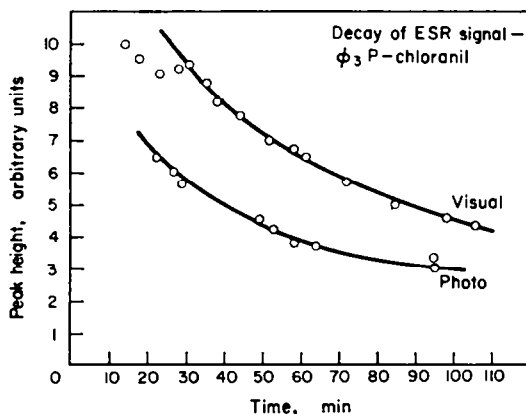
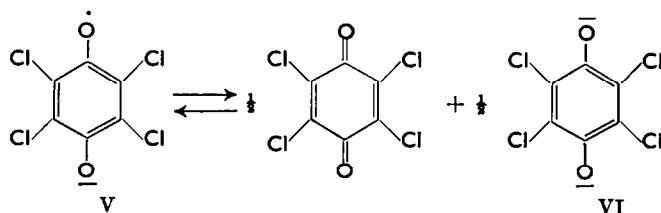


FIG. 6. Decay of ESR signal in a CH_2Cl_2 solution of chloranil + triphenylphosphine. Peak heights, h , in arbitrary units (at constant amplifier gain setting.) Peak heights \sim radical concentration since width $h/2$ does not change with time. *Visual*: heights by inspection of oscilloscope. *Photo*: heights from photographs of oscilloscope trace at long exposure times relative to sweep time.

shows the absence of chloranil semiquinone and is in agreement with the observations made in the UV absorption spectra.

The g -factor of chloranil semiquinone is such that its single line would approximately coincide with the low-field line of the doublet due to the second radical. The addition of 5% EtOH to the CH_2Cl_2 changed the character of the ESR spectrum. The initial spectrum had, now, two lines of very different intensities; the line due to the semiquinone eventually decayed leaving the previous doublet which finally disappeared as before. It does not seem unreasonable that such a change from a

completely aprotic solvent would affect the equilibria between a semiquinone (V) and a quinone plus the quinol dianion (VI).^{11c}



Regeneration of ESR spectra. When more CH_2Cl_2 solution of chloranil was added to an equimolar mixture of triphenylphosphine and chloranil in the same solvent, *shortly after admixture*, the red colour and the doublet ESR spectrum reappeared and now persisted for many hours instead of only for the few minutes observed in the initial reaction. The same effect was produced by solid PbO_2 and MnO_2 . However, if equal volumes (say 1.0 ml) of 0.01M triphenylphosphine and chloranil were mixed and *left to stand till the colour and the ESR-spectrum vanished*, the addition of 2.0 ml of 0.01M chloranil did not regenerate the radical.

If a large excess of powdered chloranil was added to the above solution radicals appeared to be formed at the surface of the solid chloranil. It was possible to generate the radicals also by addition of PbO_2 and MnO_2 to the above solution.

It seems that the dipolar ion product (III) cannot be easily oxidized by *chloranil in solution*, after all the initial reactants have been used up. However, a more difficult oxidation of the product (III) appeared to occur at the surface of *solid chloranil* or of solid inorganic oxidants like PbO_2 and MnO_2 .

To confirm this point, the *solid 1:1 adduct* (III) was prepared in benzene solution, as previously described.⁴ This solid was washed, first with benzene and then with CH_2Cl_2 , and was dried at 20° (0.1 mm); all operations were performed under nitrogen.

The free-flowing off-white solid consisted almost entirely of dipolar ion (III) as indicated by hydrolysis experiments.⁴ However, the solid was contaminated with small amounts of free radicals, since it gave a broad ESR-signal with a *g*-factor from 2.0035 to 2.0045. From comparisons with the solid free radical diphenylpicrylhydrazyl, it was estimated that the solid adduct contained about 1% of radicals.

A 1×10^{-2} M solution of this solid adduct in CH_2Cl_2 had a pale pink colour and showed a very weak ESR doublet. *There was no change in the intensity of this signal when the solution was mixed with a 1×10^{-2} M solution of chloranil in CH_2Cl_2 .* However, when a large excess of powdered chloranil was added to the CH_2Cl_2 solution of the adduct, radicals were slowly generated at the solid-liquid interface. The corresponding ESR signal was the doublet previously observed.

A saturated CH_2Cl_2 solution of the solid adduct gave no UV absorption above 340 $m\mu$ (dotted curve 1 of Fig. 7). Traces of chloranil semiquinone were noted in a fresh MeOH solution of the adduct (solid curve 3); this disappeared with time (dashed curve 4). Fig. 7 (dotted curve 2) shows also the hydrolysis of the adduct to triphenylphosphine oxide (260, 267, 273 $m\mu$) and tetrachlorohydroquinone (308 $m\mu$).

*ESR spectra of systems derived from triphenylphosphine and other tetrahalo-*p*-Benzoquinones.* The *g*-factors and hyperfine constants for the radicals formed by

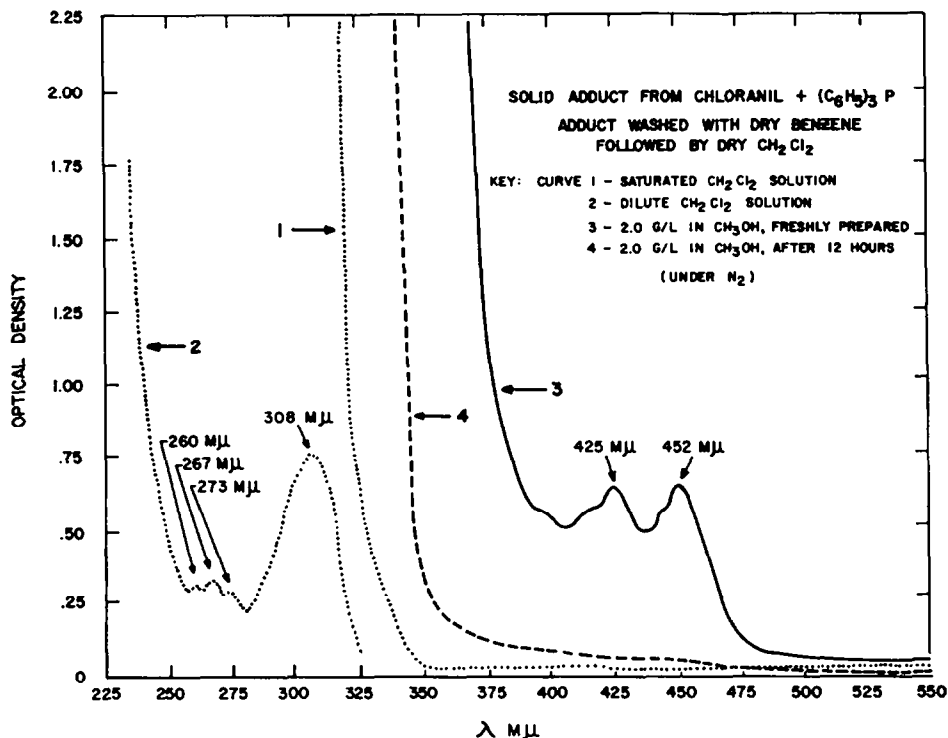


FIG. 7. Solid 1:1 *adduct* from chloranil and triphenylphosphine in dry benzene under N_2 and followed by dry CH_2Cl_2 . Curve 1, . . . , saturated CH_2Cl_2 solution. Curve 2, . . . , same solution diluted and hydrolysed to triphenylphosphine oxide and tetrachlorohydroquinone. Curve 3, —, fresh MeOH solution of adduct (2.0 g/l). Curve 4, —, same as 3 after 12 hr.

TABLE 1. *g*-FACTORS AND HYPERFINE CONSTANTS FOR THE RADICALS FORMED BY REACTION BETWEEN TRIPHENYLPHOSPHINE AND QUINONES IN SOLUTION IN CH_2Cl_2

Quinone	$g \pm 0.0001$	$\Delta H \pm 0.05$ gauss
Chloranil	2.0050	2.42
Bromanil	2.0062	2.04
Iodanil	2.0073	1.80

reactions in CH_2Cl_2 solutions are given in Table 1. It can be seen that the radical involves the quinone as well as the phosphine since both the *g*-factor and hyperfine splitting constant vary with the nature of the quinone used. The radical cannot, ^{4,7,13} therefore, be $(C_6H_5)_3P^+$.

UV spectrum of the chloranil-triethyl phosphite system. Fig. 8 shows the behaviour of chloranil with the phosphite in CH_2Cl_2 . After 10 sec (dashed curve 1) there was

¹³ P. D. Bartlett, E. F. Cox and R. E. Davis, *J. Amer. Chem. Soc.* **83**, 103 (1961).

very little reaction; (the peak at $346\text{ m}\mu$ is probably related to the reported weak $n \rightarrow \pi^*$ transition of chloranil). After 300 sec (solid curve 2) the 388, 412 and $540\text{ m}\mu$ peaks, previously seen in the phosphine case, were present, i.e., the nature of the phosphorus compound does not affect the *UV* spectrum of the species responsible for these bands.

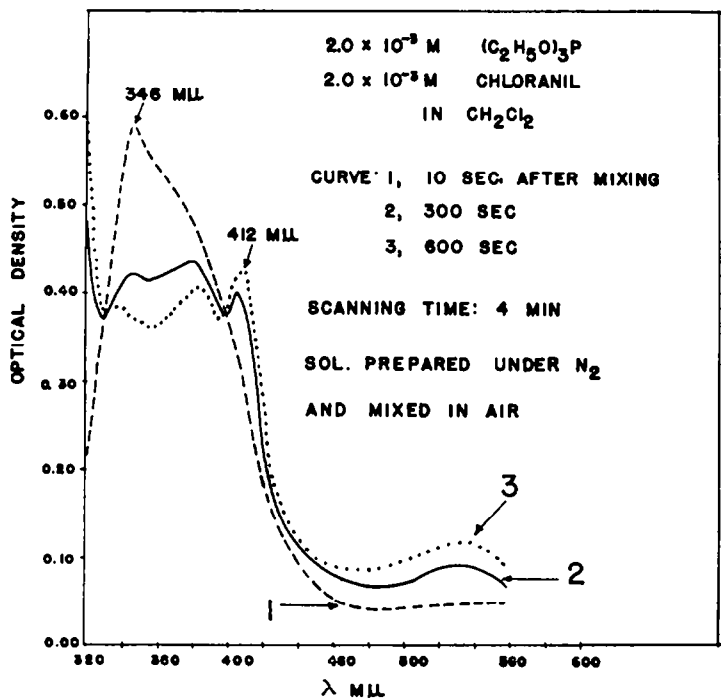


FIG. 8. A solution of $2.0 \times 10^{-3}\text{ M}$ each of chloranil and of triethyl phosphite prepared under N_2 and mixed in air in CH_2Cl_2 , at 25° ; scanning time 4 min. Curve 1, ----, after 10 sec. Curve 2, —, after 300 sec. Curve 3, . . ., after 600 sec.

The final product in this case is an alkyl ether of a *p*-quinol phosphate (VIII) which has its absorption maximum at $310\text{ m}\mu$. The phosphate (VIII) is assumed to form from the dipolar ion IX

The course of the reaction of a more concentrated solution, $1.0 \times 10^{-2}\text{ M}$ is shown in Fig. 9. Note the lack of residual absorption after 14.5 hr.

ESR spectrum of the chloranil-triethyl phosphite system. The spectrum of a red equimolar solution of chloranil and triethyl phosphite in benzene had also two peaks of equal intensity; it was in fact very similar to the chloranil-phosphine spectrum.

When two moles of triethyl phosphite in CH_2Cl_2 were added at once to one mole of chloranil suspended in CH_2Cl_2 , an immediate exothermic reaction occurred. The red solution, examined after 30 min, gave a strong ESR doublet, with both peaks of about equal intensities (Fig. 10). The *g*-factor was 2.0051, $\Delta H = 1.83$ gauss. The colour and the ESR signal vanished rapidly on exposure to air. If two drops of EtOH were introduced prior to admixture of the reagents, the red colour did not remain for more than a few seconds.

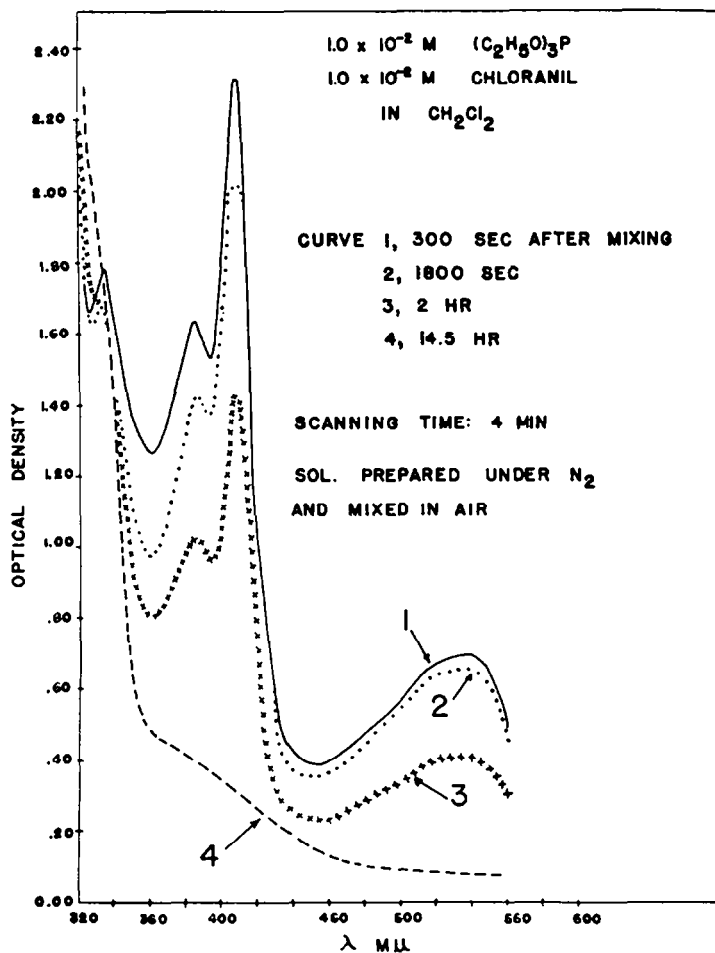


FIG. 9. Solutions of $1.0 \times 10^{-2} \text{ M}$ each of chloranil and of triethyl phosphite were prepared under N_2 and mixed in air in CH_2Cl_2 at 25° ; scanning time 4 min. Curve 1, —, after 300 sec. Curve 2, ---, after 1800 sec. Curve 3, xxx, after 2 hr. Curve 4, ---, after 14.5 hr.

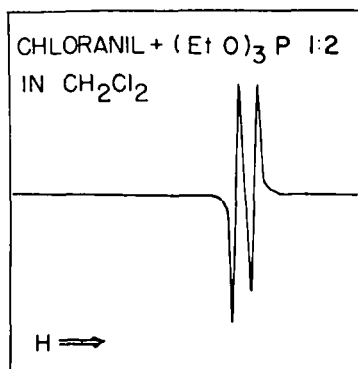
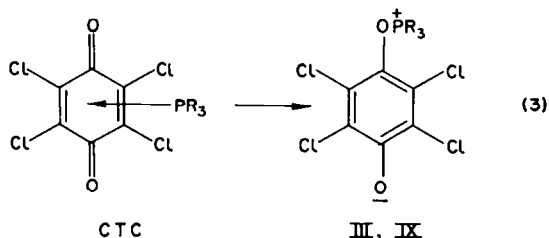
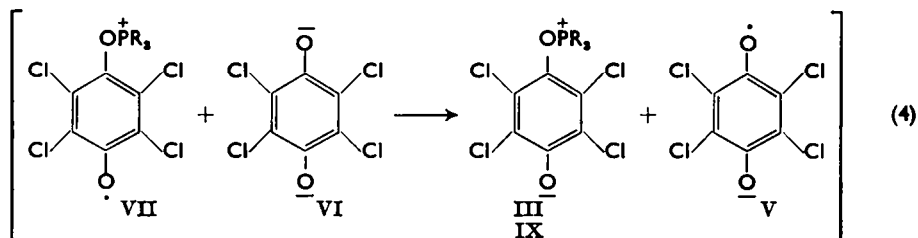


FIG. 10. ESR of the chloranil-triethyl phosphite system (1:2) in CH_2Cl_2 ($4 \times 10^{-3} \text{ M}$ in quinone), after ca. 30 min.

The *dipolar-ion products* (III or IX), may be formed in reactions which are essentially independent of the formation of the radicals, for example, by rearrangement of the CTC (Eq. 3) or by direct nucleophilic attack by phosphorus on carbonyl-oxygen, a two-electron transfer process.



The dipolar ion products (III and IX) could, conceivably, result from the reduction of the radical cation (VII) by dianion VI (Eq. 4). The semiquinone (V) is probably a more stable radical than the radical cation (VII). However, this view of the formation of the products (III and IX) is not favored because it would necessitate the formation of radicals in all those cases in which reactions of trivalent phosphorus compounds with quinones and with other polycarbonyl compounds give products with new phosphorus-oxygen bonds.¹⁴ The available evidence does not support such a generalization.



An excess of the quinone can lead to a build-up of radicals by shifting the equilibrium of Eq. 2 to the right. This is the situation that prevails, also, in the early stages of the reaction with equimolar amounts of reagents. Since the radicals come from phosphine or from CTC, and not from product III, regeneration of radicals can not occur when all the phosphine (or the CTC) has been consumed.

An assignment of structure to the species responsible for some of the UV absorption maxima can be made from certain observations and from data in the literature. The species responsible for the absorption at 515–520 $m\mu$ (in a glass at 77°K) and at 530–535 $m\mu$ (in CH_2Cl_2 solution) is probably the charge-transfer complex^{8,15} (CTC), of Eq. 1. (cf. Fig. 1).

Chloranil is known to form complexes with a number of donor molecules. The

¹⁴ F. Ramirez, *Pure and Applied Chem.* **9**, 337 (1964).

^{15a} L. Michaelis and S. J. Aranick, *J. Amer. Chem. Soc.* **66**, 1023, (1944); ^b J. Czekalla and G. Briegleb, *Z. Elektrochem.* **58**, 249 (1954); ^c J. Czekalla, G. Briegleb, W. Herre and R. Glier, *Ibid.* **61**, 537 (1957); ^d W. L. Peticolas, *J. Chem. Phys.* **26**, 429 (1957). These Refs deal specifically with chloranil. For general reviews see L. J. Andrews, *Chem. Revs.* **54**, 713 (1954), L. E. Orgel, *Quant. Revs.* **8**, 422 (1954); R. Kuhn, *Angew. Chem.* **66**, 658 (1954).

complex with hexamethylbenzene^{15a,c} has absorption maximum at 510 m μ in benzene, and at 517 m μ in CCl₄, both at 20°. The complex has a broad maximum at ca 503 m μ ^{15c,16} in an ether-isopentane glass at 77°K. The complex with dimethylaniline^{8,15a} is reported to have maxima at 345 m μ and at 645 m μ in CCl₄. However, the complex with N,N,N',N'-tetramethyl-*p*-phenylenediamine⁹ has a spectrum in acetonitrile which is a combination of the known spectra of the Würster's blue radical cation (560 and 615 m μ) and chloranil semiquinone (425 and 452 m μ). In other words, here, a complete oxidation-reduction seems to have occurred.

The absorption maximum at 412 m μ is attributed to the phenoxy-O-phosphonium radical ion (VII). This is reasonable in view of the maxima at 425 and 452 m μ for the chloranil semiquinone. *The relatively small hyperfine splitting constant of the radical-cation (VII) $\Delta H = 2.52$ gauss is to be expected since this is essentially a phenoxy radical in which the phosphonium group is separated from the ring by an oxygen atom.* Phenoxy radicals with the phosphonium group directly attached to the benzene ring have been reported.¹⁷

Disproportionations of a semiquinone into a quinone and the hydroquinone dianion have been observed in the duroquinone series.¹⁸

The origin of the band at 388 m μ which was observed in both the phosphine and the phosphite cases, in CH₂Cl₂, is not clear. It could perhaps be due to a complex between chloranil as acceptor and the dianion (VI) as donor.

The picture of the interaction between chloranil and the trivalent phosphorus compounds which has been given here stresses the oxidation potential of the quinone as the factor responsible for the formation of radicals, and of CTC. It suggests the possibility that certain quinones, or other polycarbonyl compounds, of low oxidation potential, but capable of forming CTC with trivalent phosphorus compounds, may produce coloured solutions with the latter; these solutions could still be diamagnetic. Finally, the formation of adducts with new phosphorus-oxygen bonds in these types of reactions does not presuppose, necessarily, the production of radicals in solution, although in some cases, the production of radicals may accompany the establishment of this type of bond.

SUMMARY AND CONCLUSIONS

The interaction of chloranil with triphenylphosphine and with triethyl phosphite is complex, although the nature of the final product in both cases is relatively simple. The reactions were studied in CH₂Cl₂ solution by means of ESR and UV absorption spectroscopy. In addition, the phosphine-chloranil interaction was studied also at low temps, at 77°K and in the range -70° to -25°, in CH₂Cl₂-(CH₃)₂CHCl solution, by means of UV spectroscopy. The ESR spectrum of the phosphine system was also examined in benzene and in tetrahydrofuran.

The data are consistent with a picture in which the chloranil acceptor and the phosphorus compound donor form a charge transfer complex (CTC) very rapidly. This CTC undergoes a rapid oxidation by chloranil yielding a phenoxyradical-phosphonium cation (VII) and a chloranil semiquinone (V) radical anion. The semiquinone disproportionates completely and rapidly to chloranil and tetrachlorohydroquinone dianion if the CH₂Cl₂ is scrupulously free from hydroxylic solvents and if

¹⁶ E. M. Kosower, *J. Amer. Chem. Soc.* **78**, 5700 (1956).

¹⁷ E. Müller, *Liebigs Ann.* **658**, 103 (1962).

¹⁸ N. K. Bridge and G. Porter, *Proc. Roy. Soc.* **244**, 259, 276 (1958).

air is excluded. The final product of the reaction is a dipolar ion (III) which is not susceptible to oxidation to radicals by chloranil in solution. This adduct (III) can be oxidized to radicals by solid inorganic reagents or by a large excess of powdered chloranil, but now the oxidation seems to occur at the surface of the solids.

EXPERIMENTAL

The chloranil had m.p. 290° after three crystallizations from 95% EtOH, and thorough vacuum-drying. The triphenylphosphine has m.p. 79.5–80.0 after chromatography over alumina and recrystallizations. Triethyl phosphite was freshly distilled. The CH_2Cl_2 was spectro-grade and was distilled from CaCl_2 . All substances were protected against moisture and air.

UV spectrometry at room temp. A Cary recording spectrophotometer was used. Solutions (1 ml) of the reagents were mixed in a 1 cm quartz absorption cell equipped with a tight fitting ground joint stopper. The solutions were made and mixed in a dry-box under N_2 or under air as indicated.

Low temp UV spectrometry. These experiments were carried out at the Brookhaven National Laboratory with the assistance of Dr. Simon Freed.

A Cary recording spectrophotometer was adapted to secure spectra at low temp. Attached to the spectrophotometer was a quartz Dewar flask, portions of which were not silvered to permit passage of light. A hemispherical block of Al with properly machined openings served as the cell holder. The cell itself consisted of a quartz tube about 75 cm in length, to one end of which was fused a rectangular quartz absorption cell of 1 cm path length. The other end of the tube was tightly stoppered. About 50 cm from the absorption cell was located a small side arm in which a second solution might be stored prior to admixture with a solution contained in the absorption cell itself. The entire cell plus side arm could be immersed in a large Dewar flask filled with a dry ice-acetone slurry. Thus both solutions might be precooled and then mixed by turning the side arm through a half revolution. The mixture of solutions was then transferred quickly to the smaller Dewar attached to the spectrophotometer. This bath contained trichloroethylene and was cooled by means of a copper coil through which liquid N_2 circulated.

ESR spectra. Some solutions were made and transferred in a vacuum line system equipped with a set of dropping funnels, one of which served as reaction vessel and was connected to the tube used to collect the solution for examination in the ESR spectrometer. The amounts of chloranil and of triphenylphosphine were 0.0427 millimoles each; 3 ml of CH_2Cl_2 was used. The final solution was 7.12×10^{-3} M in each reagent. The time of mixing and of spectral examinations were noted. Observations were made visually in one run, photographically in another. The rate of decay of the ESR doublet is given in Fig. 6. The photograph obtained 94.5 min after mixing is shown in curve B of Fig. 5. The peak height was 3.2 arbitrary units. The photograph obtained 29.0 min after mixing is shown in curve A of Fig. 5. The peak ht. was 5.7 arbitrary units.

In some experiments, the solutions were mixed under N_2 , but not in vacuum lines. Similar results were obtained.

Experiments with the solid chloranil-triphenylphosphine adduct (IIIa). A solution of chloranil (500 mg; 2 mmoles) in anhydrous benzene (35 ml) was added over a 4 min period to a solution of triphenylphosphine (550 mg; 2.1 mmoles) in benzene (25 ml), with stirring, under N_2 . Red colour was noted within 2 min. The solution became cloudy immediately. Considerable amounts of solid had precipitated after 1 hr. After 16 hr the solid was filtered from the pink solution. The solid was washed, first with 50 ml benzene, then with 5 portions CH_2Cl_2 (10 ml each); the last washing was nearly colourless. The off-white solid was dried for 3 hr at 20° (0.1 mm). This solid gave a single very broad ESR-signal with *g*-factor from 2.0035 to 2.0045.

A 1×10^{-3} M solution of the solid in CH_2Cl_2 gave a very weak ESR doublet. One ml of this solution was mixed with 1 ml of a 1×10^{-3} M solution of chloranil in CH_2Cl_2 . There was no change in the intensity of the ESR doublet.

Powdered chloranil was added to the solution of the solid in CH_2Cl_2 . The spectrometer was directed to the solid-liquid interface; within 2 min the intensity of the ESR doublet had doubled.

ESR of the chloranil-triethyl phosphite system. Triethyl phosphites (0.4 mmoles; kept two days over Na wire and distilled) was added to a suspension of chloranil (50 mg; 0.2 mmoles) in anhydrous CH_2Cl_2 (5 ml), under N_2 . Within 30 sec there was an exothermic reaction; the chloranil went into

the deep red solution. The ESR spectrum examined within 2 min gave a strong doublet. The red solution gave the doublet also after 30 min (Fig. 10). When the solution was allowed to come in contact with air, the colour and the signal vanished.

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