

phosphine dissolved in 10 ml. of ether was added to 1.28 g. (0.00526 mole) of diphenylphosphonyl azide in 25 ml. of ether. When the mixture was heated under reflux for 4 hr., there was a slow precipitation of a white solid. The solid was removed by filtration, washed with ether and with dilute ammonium hydroxide solution and finally vacuum dried to yield white diphenylphosphonimidotriphenylphosphorane (75.7% yield), m.p. 150–151°, after recrystallization from isopropyl alcohol and water m.p. 170–171°. *Anal.* Calcd. for $C_{30}H_{25}NOP_2$: N, 2.93; P, 12.98; mol. wt., 477.5. Found: N, 2.92; P, 13.0; mol. wt., 480. In a similar manner, bis-*p*-tolylphosphonimidotriphenylphosphorane, m.p. 176–178°, bis-*p*-chlorophenylphosphonimidotriphenylphosphorane, m.p. 205–206°, diphenylphosphonimidotris-*p*-chlorophenylphosphorane, m.p. 135–140°, and diphenylthiophosphonimidotriphenylphosphorane, m.p. 179–179.5°, were prepared and fully characterized.

Qualitatively, it appears that the rate of reaction of tertiary phosphorus compounds with diphenylphosphonyl azide to liberate nitrogen is in the order $C_6H_5P(CH_3)_2 > (CH_3O)_3P > (C_6H_5)_3P > p-(C_6H_5)_2P-C_6H_4-P(C_6H_5)_2$

There was no evidence of reaction during the attempted preparation of diphenylphosphonimidotriphenylphosphorane, $(C_6H_5)_2PN=P(C_6H_5)_3$, by the *in situ* reaction of chlorodiphenylphosphine, sodium azide, and triphenylphosphine in pyridine at 115°. However, when diphenylphosphonyl chloride was added to a mixture of triphenylphosphine and sodium azide in pyridine at 115°, there was a rapid evolution of nitrogen and diphenylphosphonimidotriphenylphosphorane was obtained in a quantitative yield. Unexpectedly, the *in situ* reaction with diphenylthiophosphonyl chloride did not yield the diphenylthiophosphonimidotriphenylphosphorane, but gave an 87% yield of triphenylphosphine sulfide and the same diphenylphosphinic nitride polymer mixture (Equation 3) previously reported by Herring^{1,5} from $(C_6H_5)_2P(S)Cl + NaN_3 + (C_6H_5)_3P \rightarrow (C_6H_5)_3PS + [(C_6H_5)_2PN]_{2,4}$ (3)

which diphenylphosphinic nitride tetramer has been isolated. The tetramer was characterized by comparison with authentic material.⁶

This unexpected reaction is being investigated further. In addition, the azides and corresponding phosphoranes of Groups III, IV, V, and VI are under active investigation.

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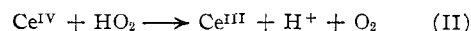
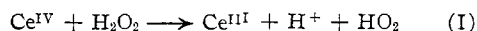
(6) We wish to thank Mr. D. L. Herring, U. S. Naval Ordnance Laboratory, Corona, Cal., for the sample of diphenylphosphinic nitride tetramer and its infrared spectrum.

THE ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF THE HO_2 RADICAL IN AQUEOUS SOLUTION¹

Sir:

In a recent note J. W. T. Spinks² reported an e.p.r. spectrum of what is believed to be the HO_2 free radical in solid ice at liquid nitrogen temperature. We wish to support his findings by a similar e.p.r. spectrum obtained in an aqueous solution at room temperature.

The basis of our experiment is the generation of HO_2 when ceric sulfate interacts with hydrogen peroxide in strong acid solutions. This reaction has been known in analytical chemistry for some time³ and has been reinvestigated independently by Stein⁴ and Anbar.⁵ While Stein postulates that the reaction takes place in two steps



Anbar proposes as an intermediate the complex $Ce^{III} \cdot OOH$.

The set-up used in the present investigation consists of a flow-system with a mixing chamber located 0.5 cm. above the cavity of a Varian EPR Spectrometer. The mixed solutions flow through a quartz tube which passes through the center of the cavity. The flow velocity of the solutions can be varied over a wide range.

When a 0.001 *M* ceric sulfate solution is mixed with a 0.1 *M* solution of hydrogen peroxide, an e.p.r. spectrum is obtained as shown in Fig. 1.

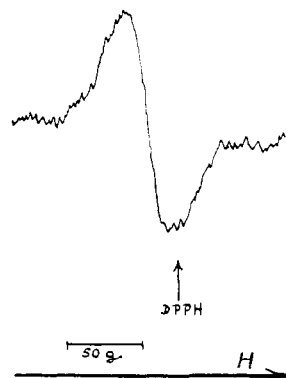


Fig. 1.—E.p.r. spectrum of the HO_2 radical produced during the interaction of $Ce(HSO_4)_4$ with hydrogen peroxide in 0.8 *N* sulfuric acid solution; vertical line indicates the position of DPPH signal.

The *g* for this species is 2.016 with a line width of 27 gauss. The magnitude of the spectrum is a function of the flow velocity as well as the concentration of solute in the solutions. When the flow of the solutions is stopped while in the cavity, the spectrum disappears rapidly. The individual solutions or an aged mixture of the two gave only background noise.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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(3) Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 8th Ed., Vol. II, p. 752.

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Although a quantitative study of the ceric sulfate, hydrogen peroxide reaction by Stein⁴ rules out the existence of other radicals in addition to the HO₂, it does not elucidate whether this species is present in the free or complexed form. Since, according to Anbar,⁵ the cerous ion is capable of complexing the free HO₂, an experiment was carried out with an excess of cerous sulfate in the flow mixture. The resulting e.p.r. spectrum showed a significant decrease in signal strength as well as a change in line width. The change in signal strength can be due either to the formation of a diamagnetic complex or a back-reaction. Either case accounts for the decrease in free radical concentration. The decrease in line width may be the result of "exchange narrowing."

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THE ATOM POLARIZATION OF *p*-BENZOQUINONE FROM INFRARED INTENSITIES

Sir:

Dielectric polarization studies of *p*-benzoquinone¹⁻⁶ have shown a large difference between the total polarization, P_T , and the electronic polarization, P_E , determined from the index of refraction in the visible. The difference $P_T - P_E$ is usually ascribed to atomic polarization, P_A , and to orientation polarization for molecules possessing a permanent dipole moment. For *p*-quinone $P_T - P_E$ is 8.2 cc.⁵ or about 28% of P_E , whereas P_A alone is normally expected to be about 5-10% of P_E . This discrepancy, together with some ambiguity in the temperature dependence of P_T , has led some investigators¹⁻⁴ to propose that *p*-quinone has a dipole moment of about 0.7 debye. Recently⁷ it was demonstrated conclusively by electrooptic birefringence measurements that, as expected from the centro-symmetry of its structure, this molecule does not have a permanent dipole moment (larger than 0.15 debye). The birefringence study also showed that the large difference of $P_T - P_E$ is not caused by an anomalous field induced moment arising from a lack of orbital following of the non-bonding carbonyl electrons as has been proposed.⁸ It was concluded in accord with an earlier suggestion by Coop and Sutton⁵ that the entire difference in the polarization very probably resulted from an unusually high atomic polarization.

Dispersion theory can be used to relate the atomic polarization to the intensities of absorption bands in the infrared region of the spectrum.^{9,10}

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(5) I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

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In connection with a detailed study of the vibrational spectra of quinone and its deuterated derivatives,¹¹ we have measured the intensities of those infrared bands which contribute significantly to the atomic polarization. These bands are listed in Table I, together with the contribution of each to the atomic polarization, P_{A_j} . The polarizations are calculated from the equation given by Whiffen¹⁰ in the modified form

$$P_{A_j} = (3\pi^2\nu_j)^{-1}\Gamma_j \quad (1)$$

$$\Gamma_j = \nu_j^{-1} \int \alpha_\nu d\nu \quad (2)$$

where $\int \alpha_\nu d\nu = (Cl)^{-1} \int \ln(I_0/I) d\nu$, ν is in cm.⁻¹, the concentration C in moles/liter and the cell length l in cm. ν_j is the frequency in cm.⁻¹ of the j 'th absorption band, and the total atomic polarization is $P_A = \sum_j P_{A_j}$. The units yield the intensities Γ_j in cm.² mol.⁻¹ as recommended by Mills.¹²

TABLE I

Band, ^a cm. ⁻¹	Intensity (cm. ² mol. ⁻¹)	P_{A_j} , cm. ² mol. ⁻¹
1664	9,670	0.21
1303	2,150	.06
1068	1,500	.05
946	650	.03
882	4,480	.17
409	6,010	.50
108	19,080	5.95

$$\sum P_{A_j} = 6.97$$

^a All bands were measured in benzene except the 409 cm.⁻¹ band which was measured in CCl₄. The intensity listed for 1664 cm.⁻¹ is that of all the absorption in that region including the very low intensity band at 1591 cm.⁻¹ with the center of gravity taken as that of the intense bands near 1664 cm.⁻¹. The errors of measurement far outweigh any errors from this approximation. Spectral slit widths were always considerably less than bands widths, and no correction was applied for the effects of finite resolution. Concentrations were in the range 0.1-0.3 molar.

The difference $P_T - P_E$ is reported by Hammick, *et al.*,⁶ as 8.8 cc. (in C₆H₆), 9.6 cc. (in CCl₄) and 8.7 cc. (in *n*-hexane); by Meredith, *et al.*,⁴ as 9.1 cc. (25° in C₆H₆); and by Coop and Sutton⁵ as 8.2 cc. (vapor). From the data in Table I, $P_A = 7.0$ cc. In view of the scatter of dielectric data and experimental uncertainties in the infrared data (including solvent effects on the intensities), we consider the agreement between P_A and $P_T - P_E$ excellent. *There seems to be no further room for doubt that the large polarization difference is substantially accounted for by the atom polarization.*

The ν_j^{-2} factor obtained by combining equations (1) and (2) makes low frequency bands especially important in calculating atomic polarization. It is observed that the band at 108 cm.⁻¹ makes by far the largest contribution, 5.95 cc. Anno and Sadô¹³ assign this band to a b_{1u} (out of plane) ring distortion. We concur in the assignment as a b_{1u} fundamental, but on the basis of its intensity and analogies to similar molecules we believe that the vibration is largely due to out of plane C=O motion.¹⁴

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