

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}

- (1) O. Hassel and E. Naeshagen, *Z. physik. Chem.*, **B6**, 441 (1930).
- (2) D. L. Hammick, G. C. Hampson and G. I. Jenkins, *Nature*, **136**, 990 (1935).
- (3) C. J. Lefevre and R. J. W. LeFevre, *J. Chem. Soc.*, 1696 (1935).
- (4) C. C. Meredith, L. Westland and G. F. Wright, *J. Am. Chem. Soc.*, **79**, 2385 (1950).
- (5) I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).
- (6) D. L. Hammick, G. C. Hampson and G. I. Jenkins, *ibid.*, 1263 (1938).
- (7) E. Charney, *J. Am. Chem. Soc.*, **83**, 578 (1961).
- (8) L. Pauloni, *ibid.*, **80**, 3879 (1958).

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

- (9) K. H. Illinger and C. P. Smyth, *J. Chem. Phys.*, **32**, 787 (1960).
- (10) D. H. Whiffen, *Trans. Faraday Soc.*, **54**, 327 (1958).
- (11) To be published later.
- (12) I. M. Mills, *Chem. Soc. Ann. Reports Prog. Chem.*, **55**, 55 (1958).
- (13) T. Anno and A. Sadô, *Bull. Chem. Soc. Japan*, **31**, 734 (1958).

This study indicates the major role which a low frequency vibrational mode with moderately large transition moment plays in the static polarizability of quinone. The results suggest that similar behavior may be found in other molecules, especially some of those discussed by Meredith, *et al.*,⁴ and Hammick, *et al.*,⁵ which have anomalously large $P_T - P_E$.

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(14) This band was found by Cartwright and Errera at 120 cm^{-1} , as reported by Hammick, *et al.*⁵ Coop and Sutton,⁶ together with Hammick, *et al.*, suggested correctly that this band makes a significant contribution to the atomic polarization and attempted to interpret the infrared datum in terms of one dimensional oscillators. They were forced to assume the existence of two independent *in plane* oscillators to obtain agreement with the observed frequency.

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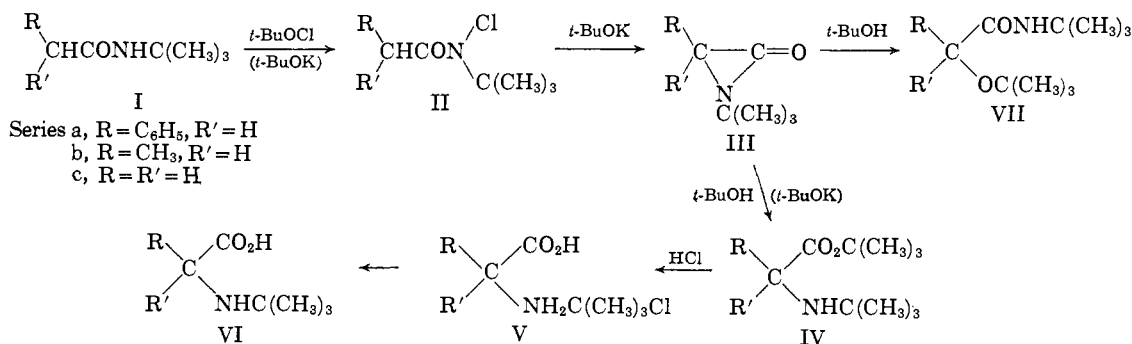
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REACTIONS OF AMINES. IX. THE
REARRANGEMENT OF N-*t*-BUTYL-N-
CHLOROAMIDES^{1,2}

Sir:

Sheehan and Frankenfeld³ have established that, although they probably are intermediates in the Favorskii-like, sodium hydride-catalyzed rearrangement of certain α -chloroanilides, azirdinones (α -lactams) are not found among the final products of the rearrangement, as claimed earlier by Sarel and Leader,⁴ but are converted under the conditions employed to oxindole and indoxyl derivatives. This communication describes the formation of α -*t*-butylaminoacids (VI) through the Favorskii-like rearrangement of N-*t*-butyl-N-chloroamides (II) and offers presumptive evidence for the existence of α -lactams (III) as moderately stable intermediates under the more favorable conditions of this rearrangement.



In a typical experiment N-*t*-butylphenylacetamide (Ia) ($\nu(\text{C}=\text{O})$ 1647 cm^{-1} (KBr); $\nu(\text{C}=\text{O})$ 1661 cm^{-1} , $\nu(\text{N}-\text{H})$ 3420 cm^{-1} (CHCl₃) was

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(2) Part VIII, *J. Org. Chem.*, **26**, 1533 (1961).

(3) J. C. Sheehan and J. Frankenfeld, *J. Am. Chem. Soc.*, **83**, in press (1961).

(4) S. Sarel and H. Leader, *ibid.*, **82**, 4752 (1960).

converted into N-*t*-butyl-N-chlorophenylacetamide (IIa) ($\nu(\text{C}=\text{O})$ 1670 cm^{-1} (CHCl₃)) by treatment with *t*-butyl hypochlorite and a trace of potassium *t*-butoxide. In general the N-chloroamide was not isolated but was rearranged by addition *to* potassium *t*-butoxide (in *t*-butyl alcohol) or by addition of the same reagent. In the former instance the N-chloroamide was added to two equivalents of cold potassium *t*-butoxide giving, after isolation, a crude ester (presumably IVa) ($\nu(\text{C}=\text{O})$ 1749 cm^{-1} (liquid film)) as a viscous oil. Hydrolysis of the ester with concentrated hydrochloric acid gave a 72% yield of N-*t*-butylphenylglycine hydrochloride (Va) (as the methanolate, m.p. 207-208° (dec.) with a characteristic gas evolution (loss of methanol?) at 126-127°, from methanol-ether; found for C₁₃H₂₂NO₃Cl: C, 57.05; H, 7.87; N, 5.23). The yield of Va from once-distilled IIa was 68%. The free amino acid VIa could be obtained by ion exchange (m.p. 152-153°; found for C₁₂H₁₇NO₂: C, 69.33; H, 8.34; N, 6.40). Both products were identical with authentic samples prepared by the Strecker synthesis.

By similar treatment N-*t*-butylpropionamide (Ib) and N-*t*-butylacetamide (Ic) gave 49 and 30% yields of N-*t*-butylalanine (VIb) and N-*t*-butylglycine (VIc), respectively (VIb, m.p. 201-202°; found for C₇H₁₆NO₂: C, 57.67; H, 10.49; N, 9.80. VIc methyl ester hydrochloride, m.p. 171-172°; found for C₇H₁₆NO₂Cl: C, 46.05; H, 8.88; N, 7.43).

In several experiments the course of the reaction was followed by periodic infrared analysis of samples from the reaction mixture. Dropwise addition over a 2-hr. period of 0.1 mole of potassium *t*-butoxide in 100 ml. of *t*-butyl alcohol to a cold solution (ice-bath) of 0.1 mole of Ia and 0.1 mole of *t*-butyl hypochlorite in 225 ml. of benzene caused these spectral changes. Upon addition of the first few drops of base, there was a slight high-frequency shift due to N-chlorination. Continued addition of base caused a band to appear at 1847 cm^{-1} . This band grew in intensity as base was added while the band at 1670 cm^{-1} broadened somewhat

and decreased in intensity. The intensity of the 1847 cm^{-1} band reached a maximum when just slightly less than one equivalent of base had been added. Addition of further base caused a sudden marked change in the color of the solution (from pale blue-gray to pale tan), complete disappearance of the 1847 cm^{-1} band and the appearance of an ester carbonyl band at 1749 cm^{-1} (see Fig. 1).