Solution Spectra of the Species O_2^-

By W. SLOUGH

(*Organic Chemistry Division, National Chemical Laboratory, now with Basic Physics Division, National Physical Laboratory, Teddington, Middlesex*)

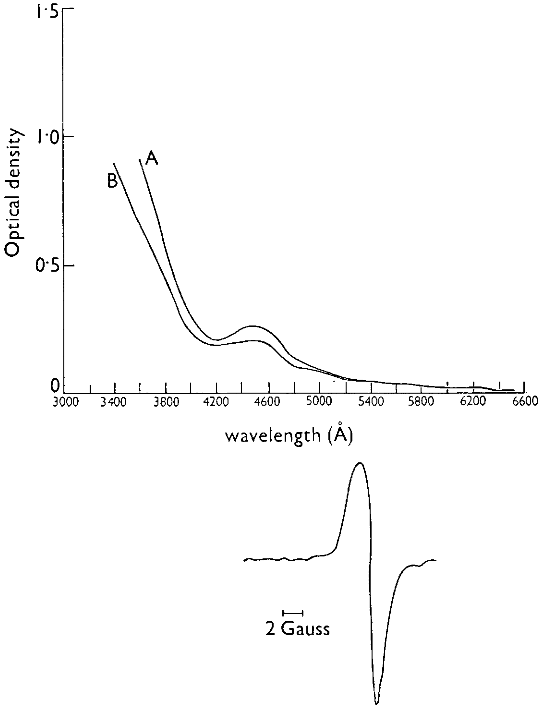
IN conjunction with an electrochemical preparation and identification (*cf.* M. E. Peover and B. S. White, accompanying Communication), ultraviolet and electron spin resonance absorption spectra have been recorded for O_2^- in dry pyridine solution with tetrabutylammonium perchlorate as supporting electrolyte. A difference method was used to record the ultraviolet absorption spectra in which the spectrum of the solution containing O_2^- was determined relatively, with electrolyte in pyridine as the blank solution. This method loses sensitivity when the absolute absorption of the pyridine becomes too great and therefore spectra are not recorded below 3400 Å. The ultraviolet and visible absorption spectrum of O_2^- in pyridine has a band of high intensity with $\lambda_{max} = 4425$ Å (2·80 ev.). Both bands are reduced in intensity as the radical decays. The optical density at 3600 Å 30 min. after preparation is about two-thirds of the value immediately after preparation, and after 24 hr. a small residual absorption remains. This is probably due to the absorptions of products from the radical reaction. An optical absorption observed near 4·9 ev has been attributed to O_2^- centres contained in alkali-metal halide crystals,[1] and could correspond to the transition above 3·75 ev presently inferred in pyridine solution. The band at 2·80 ev is not easily accounted for by consideration of possible electronic transitions in O_2^- or in pyridine. It seems probable that this is a charge-transfer band, where the species O_2^- behaves as donor, and the pyridine molecule as

---

[1] W. Kanzig and M. Cohen, *Phys. Rev. Letters*, 1959, **3**, 509.

acceptor. The complex is represented by the two canonical structures py·O_2^- and py$^-$·O_2. Complex formation may stabilize the O_2^- species leading to the relatively slow decay observed. In accord with this the electronic spectrum of O_2^- in a solvent with feeble acceptor ability such as dimethylformamide showed no absorption maximum below 3·88 ev.

A single-line electron spin resonance spectrum of the pyridine solution was recorded with marked asymmetry, and a line width of 2·4 gauss. No hyperfine structure was shown, in agreement with the zero nuclear spin of ^{16}O. The g factor, measured by comparison with αα-diphenyl-β-picrylhydrazyl (g = 2·0036), was 2·020. This is above the free electron value of 2·0023 as expected from the possibility of mixing of excited states formed by inner electron promotion to the incompletely filled $(\pi g\ 2p)^3$ orbital.[2] For solid sodium and potassium superoxides values of $g_{\|} = 2{\cdot}175$ and $g_{\perp} = 2{\cdot}002$ have been recorded.[3] Since the mean value of these is 2·060 the present value recorded in pyridine is appreciably lower than might have been expected. This is consistent with donor–acceptor interaction in which the negative charge of O_2^- is delocalized on to the pyridine molecule. The asymmetric line-shape may also be a consequence of complex formation. In dimethylformamide a symmetric signal was recorded with a line width of 1·57 gauss. Decay of the radical could be followed by the reduction in signal intensity with time, and 24 hr. after preparation no detectable signal remained.



Ultraviolet and electron spin resonance absorption spectra of O_2^- *in pyridine.*

A = Immediately after preparation, B = 60 *minutes after preparation.*

(*Received, April* 23*rd*, 1965.)

M. Symons, *Adv. in Chem.*, No. 36, A.C.S., Washington, 1962, 80.

[3] J. Bennet, D. Ingram, M. Symons, P. George, and S. Griffith, *Phil. Mag.*, 1955, **46**, 443.