

a 60 but was retained on an 80-mesh screen was used as the column packing. Of the original 33 wt. per cent added to the mixture, 28 wt. per cent of the flour was retained on the 'Chromosorb'.

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¹ Kyriacos, G., and Boord, C. E., *Anal. Chem.*, **29**, 787 (1957).

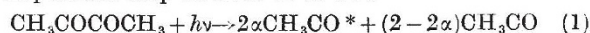
Electron Paramagnetic Resonance Spectrum of the Acetyl Radical

THE electron paramagnetic resonance (EPR) spectrum of the acetyl radical, $\text{CH}_3\text{CO}\cdot$, has been detected during and after photolysis of biacetyl at 77° K. Small (100 mg) samples of biacetyl were distilled into thin-walled quartz tubes and degassed. The samples were placed in the V-4546 quartz Dewar accessory of a Varian V-4500 spectrometer, and irradiated under liquid nitrogen with a low-pressure mercury arc.

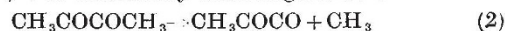
A typical spectrum, recorded after 90 min irradiation, is reproduced in Fig. 1. This spectrum was analysed in terms of two radical species each exhibiting hyperfine interaction with three equivalent protons. The wider spectrum, in which the proton hyperfine interaction is 66 ± 5 Mc/s, was attributed to the methyl radical, since the observed hyperfine splitting and g -value (2.0027 ± 0.0008) are in excellent agreement with previous work^{1,2} on the methyl radical. The features of the spectrum due to the methyl radical decreased slowly in intensity when the lamp was turned off, reaching half-intensity in approximately 15 min. The remaining spectrum, which is believed to be that of the acetyl radical, did not decay significantly after switching off the lamp, but on warming to approximately 140° K in a V-4547 variable temperature accessory, it decreased rapidly in intensity without change in shape. The hyperfine interaction is that of three protons with equal couplings of 47 ± 5 Mc/s, appreciably less than that to be expected from equivalent protons β to a π -electron radical centre³. Acetyl, which has not previously been detected spectroscopically, is a σ -electron radical analogous to the formyl radical reported recently⁴. The g -value of the acetyl spectrum was found to be 2.0055 ± 0.0008 and the comparatively high maximum-slope line-width of 15 Mc/s probably reflects a small anisotropy in the coupling constants, rather than in the g -value, since the spectrum of acetyl was quite accurately centro-symmetric.

The presence of both acetyl and methyl radicals in irradiated, condensed biacetyl is consistent with the

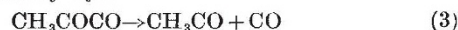
mechanism of Noyes *et al.*^{5,6}, who proposed the primary decomposition step at 2700 Å to be:



where $\text{CH}_3\text{CO}\cdot$ decomposes almost immediately into $\text{CH}_3 + \text{CO}$. Their evidence suggested that α was 0.5, and therefore (1) was kinetically indistinguishable from:

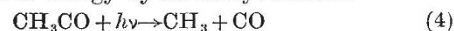


followed immediately by:



In our experiments the observed concentration of acetyl radicals was at least five times that of the methyl radicals, and even allowing for the disappearance of methyl radicals during irradiation, an upper limit of 0.25 can be placed on α of reaction (1). Therefore under our conditions reaction (2) cannot be the only primary decomposition step.

If the acetyl radical concentration were sufficiently high, a methyl radical could be formed on absorption of a second quantum of energy by an acetyl radical:



However, the build-up of methyl radicals on irradiation of biacetyl is simultaneous with that of the acetyl radicals, so that absorption by acetyl radicals cannot be the (sole) precursor to methyl radical formation.

If, as is generally believed, radical recombination reactions have very low or zero activation energies, the persistence of acetyl radicals in biacetyl at 77° K indicates that these radicals are rigidly held in the matrix. In contrast, the methyl radicals are presumably free to migrate. Further work to determine the fate of the methyl radicals is in progress, and the investigation is being extended to include higher ketyl radicals.

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⁶ Noyes, jun., W. A., Porter, G. B., and Jolley, J. E., *Chem. Revs.*, **56**, 49 (1956).

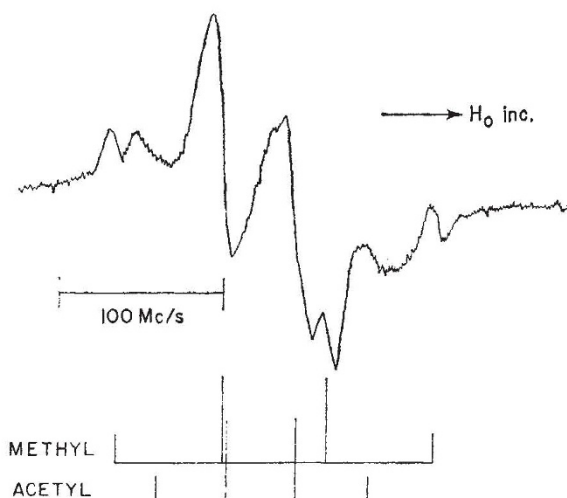


Fig. 1. EPR spectrum of ultra-violet-photolysed biacetyl at 77° K

Estimation of Small Amounts of Sulphate by Precipitation with Radioactive Barium

IN the course of work on the metabolism of sulphur amino-acids in malnourished infants it was necessary to measure total sulphate concentration in large numbers of urine samples. The urine from these patients is very dilute, so that to obtain accurate results by the classical gravimetric or titrimetric methods it would be necessary to use large volumes. This is inconvenient, since for the oxidation of organic sulphur the urines have to be digested with concentrated acid. By precipitating with barium chloride containing radioactive barium, and measuring the radioactivity in the precipitate, the estimation could be made on 0.1–0.5 ml. urine.

To a sample of 0.5 ml. containing 0.5–20 μM sulphate are added 1–2 ml. of barium chloride reagent. 1 ml. of the reagent is enough for quantities of sulphate up to 5 μM ; for quantities between 5 and 20 μM 2 ml. should be added. The reagent consists of 0.03 M barium chloride in 1 N hydrochloric acid and 60 per cent ethyl alcohol. To this is added $^{133}\text{Ba Cl}_2$, about 0.05 $\mu\text{C}/\text{ml.}$, depending on the sensitivity of the counter. The alcohol is added to reduce the solubility of the barium sulphate¹. If the solution is