Fig. 2. Absorption spectrum attributed to benzosemiquinone
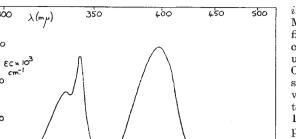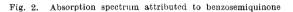
via the excited quinone molecule by hydrogen abstraction from the solvent, and be stable enough to survive further hydrogen abstraction from the solvent over the period during which it is observed. Its long life in viscous paraffin again indicates a diffusion-controlled bimolecular reaction of removal.

Detailed kinetic studies of these and related radicals in solution are in progress and will be reported later.

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[1] Porter, G., and Wright, F. J., Trans. Farad. Soc., 51, 1469 (1955).
[2] Norman, I., and Porter, G., Proc. Roy. Soc., A, 230, 399 (1955).
[3] Porter, G., and Strachan, E. (in course of publication).
[4] Herzberg, G., and Shoosmith, J., Can. J. Phys., 34, 523 (1956).
[5] Linschitz, H., Rennert, J., and Korn, T. M., J. Amer. Chem. Soc., 76, 5839 (1954).

Point of Attack in Hydrocarbon Oxidation

A CONFLICT apparently exists between the aldehyde degradation mechanism indicated by the recent findings of Bailey and Norrish[1] and of Knox and Norrish[2], on one hand, and the preferential attack at the tertiary and secondary carbon atoms deduced, indirectly, by Walsh[3], Boord[4] and Badin and Pease[5]. A possible solution is provided by some recent studies, by gas-phase chromatography, of the products of slow oxidation of n-heptane, in a flow system. Although no tests for formaldehyde were made, aldehydes from C_2 to C_6 were detected at 300° C. ; at 280° C., however, the extent of reaction was very small, and the only products condensed at − 80° C., apart from traces of peroxides, consisted of propionaldehyde and n-butyraldehyde. This suggests that the initial attack is at one of the secondary carbon atoms, with subsequent fission of one of the central C—C bonds. The more reactive chain carriers formed during this process can then attack the primary carbon also, and lead to the formation of higher aldehydes.

This deduction is supported by preliminary results obtained during studies of the partial, slow reaction of mono-deuterated propanes with a small proportion of oxygen. By carrying out kinetic studies,

in situ, on an infra-red spectrometer (Burt and Minkoff[6]), conditions were selected which avoided fission of the C—C—C skeleton. The deuterium content of the liquid products was then determined, using an infra-red method. From experiments with $CH_2D.CH_2.CH_3$ and $CH_3.CHD.CH_3$, and making some assumptions which are discussed below, it was deduced that at 360° and at 420° C., attack on the secondary C—H or C—D bond was at least 1·9 times faster than that on the corresponding primary bond.

Two of the assumptions are not likely to affect the conclusions appreciably. The first is that the relative amounts of OH and OD bonds formed are proportional to the rates of attack at each CH and CD bond in the original molecule, and the second involves the supposition that there is little, if any, difference in the isotope effect on the rate at the different positions. The third possible source of error requires more detailed consideration : at first sight, it might be expected that the formation of propylene from a propyl radical must involve the loss of hydrogen from a carbon adjacent to that at which attack initially occurred. Thus, if both steps involve oxygen, the deuterium content of the water should not permit an experimental distinction. However, it can be shown that if this were true the D : H ratios would differ considerably from those which were observed. It must therefore be deduced that the formation of propylene from the propyl radical, under the present conditions of large excess of hydrocarbon, involves reactions with radicals or molecules which contain no oxygen. Further experiments are in progress to confirm and extend these results.

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[1] Bailey and Norrish, Proc. Roy. Soc., A, 212, 311 (1952).
[2] Knox and Norrish, Proc. Roy. Soc., A, 221, 151 (1954).
[3] Walsh, Trans. Farad. Soc., 42, 269 (1946).
[4] Boord, Third Symp. on Combustion, 416 (Williams and Wilkins, Baltimore, 1949).
[5] Badin and Pease, Third Symp. on Combustion, 384 (Williams and Wilkins, Baltimore, 1949).
[6] Burt and Minkoff, Anal. Chim. Acta, 16, 259 (1957).

Micelles of Long Life : a Step towards Biological Organization

INVESTIGATIONS into the state of solution of paraffin-chain salts have usually ignored the question of the life-time of the individual aggregates (micelles)[1]. Their size is known to be limited, and they are in strict equilibrium with the free long-chain ions in solution[2]. It would appear to follow that their number fluctuates about a mean, and that the life-time of any one micelle, while small, is not capable of exact definition, especially if there is a range of sizes up to the maximum.

It is known that the size limitation may apply to one or two dimensions only ; the presence of very large aggregates is shown by the high viscosities of