pointed out, I believe, by G. E. Briggs[7]. It is highly improbable that photosynthesis depends on a single photo-reaction of unit quantum efficiency, since it would appear that there is no quantum in the visible spectrum large enough to meet the minimal energy requirement. Experimental measurements[7,8] indicate a possibility of a value as low as $0 \cdot 2$ for the overall reaction. It seems to me that we must, therefore, assume either a photo-reaction not obeying the Einstein rule, or a series of n photo-reactions (n might be as high as 5), or a gain of energy in a thermal reaction. Since the great bulk of the light falling on a leaf is transformed to heat, there is no difficulty about a source of such energy. The first two of these alternatives certainly would, and the third might, necessitate changes in the proposed schemes.

It is impossible to contemplate this field of work without wondering whether the present position justifies the application of some of the kinetic assumptions employed. Realising the approximations and 'idealisations' inevitable, it is amazing that prediction gets as near the truth as it sometimes does. In such complicated systems the possibilities of errors compensated into rough agreements appear manifold. Recent careful work[9] even makes doubtful the existence within the plant of the 'steady states' which are the very basis of the analyses quoted by the correspondents in NATURE. It is clear that 'diffusion', 'reaction' and other 'constants' cannot here be given their usual significances, if only because they differ from plant to plant. It would appear that much pedestrian work on specific plants remains to be done before we can approach accurately based semi-quantitative generalisations.

W. O. JAMES.

Department of Botany,
Oxford.
June 21.

[1] Baly and Morgan, NATURE, **133**, 414 ; 1934.
[2] Burk and Lineweaver, NATURE, **135**, 621 ; 1935.
[3] Emerson and Green, NATURE, **134**, 289 ; 1934.
[4] James, *Proc. Roy. Soc.*, B, **103**, 1 ; 1928.
[5] van den Honert, *Rec. Trav. Bot. Néerl.*, **27**, 149 ; 1930.
[6] James, *New Phytol.*, **33**, 8 ; 1934.
[7] Briggs, *Proc. Roy. Soc.*, B, **105**, 1 ; 1929.
[8] Warburg and Negelein, *Biochem. Z.*, **103**, 118 ; 1920.
[9] Harder, *Planta*, **20**, 699 ; 1923.

Thermal Decomposition of Ozone

RECENTLY, H. J. Schumacher[1] has given his reasons for regarding the interpretation of the results obtained by me[2] as incompatible with the findings of other investigators. The essential difference between these results[2] and those of Glissmann and Schumacher[3] lies in the absolute rates of decomposition. It is possible that in the vessel employed, part of the measured decomposition was due to surface activation, the ratios of rates for the different temperatures yielding an apparent heat of activation (19,000 cal.) less than the recognised endothermic heat of reaction of the gas reaction (24,000 cal.). The 'inert gas' effects, however, both accelerating and retarding, can scarcely be related to a surface decomposition in itself, but must be gas phase processes.

The calculation of the heats of activation Q_2 (reaction $O + O_3 = 2O_2$) and Q_3 ($O + O_2 + O_2 = O_3 + O_2$) from my data was based on the assumption that the number of effective collisions was given by $Ze^{-E/RT}$, the steric collision factor being taken as unity. The values thus obtained are maximum values ; correspondingly, if the heat of activation of the ternary collision is zero, the heat of activation of the secondary

reaction is 9,000 cal. The correspondence between this figure and that cited by Schumacher from photochemical data (5,000 cal.) was taken as support for the oxygen atom theory, in view of the fact that the former value was calculated on principles of diffusion not involved in the photochemical decomposition.

The region in which the postulated diffusion effect can be experimentally realised is a small one, determined by temperature as well as by pressure and vessel dimensions. The interpretation of the present results is not regarded as incompatible with the photochemical decomposition from this point of view.

It appears from the summary of Schumacher[4] that the possibility of reaction chains involving excited oxygen molecules depends largely on the nature of the oxygen atom, in the sense that the excited oxygen atom produced by photo-dissociation of ozone by light of short wave-length is more likely to start a chain than is the normal unexcited atom. When the heat of activation is close to the endothermic heat of reaction, one cannot deduce with certainty that a chain mechanism must play a large part in the thermal decomposition. Since my experiments were carried out with pressures of ozone not greater than 100 mm., and for the most part in the presence of nitrogen which would presumably tend to deactivate excited oxygen molecules, the possibility of reaction chains playing a prominent part in the decomposition in such circumstances is regarded as a small one.

MOWBRAY RITCHIE.

Department of Chemistry,
University,
Edinburgh.

[1] *Proc. Roy. Soc.*, A, **150**, 220 ; 1935.
[2] *Proc. Roy. Soc.*, A, **146**, 848 ; 1934.
[3] *Z. phys. Chem.*, B, **21**, 323 ; 1933.
[4] *J.A.C.S.*, **52**, 2377 ; 1930.

The Free *n*-Propyl Radical

THE clean fission of the lower aliphatic ketones effected by ultra-violet light led us to examine the symmetrical di-*n*-propyl ketone with the object of preparing the *n*-propyl radical.

We allowed the ketone to stream through a transparent silica tube, and irradiated it over a restricted area with the unfiltered light from two quartz mercury vapour arcs. Free radicals were produced, and rapidly removed metallic mirrors situated 10 cm. from the nearer edge of the illuminated zone.

The volatile products resulting from the action of the radicals on mercury were passed into mercuric bromide, the excess of ketone distilled off, and the solids subjected to fractional sublimation in a vacuum. The three head fractions melted at 137°–138° (mercury *n*-propyl bromide, m.p. 138°)[1]. The melting point of the fourth fraction was not depressed by admixture with an authentic specimen of mercury *n*-propyl bromide.

It is thus concluded that di-*n*-propyl ketone is decomposed in ultra-violet light with the formation of free *n*-propyl radicals.

T. G. PEARSON.
R. H. PURCELL.

Imperial College of Science
and Technology,
London, S.W.7.
June 27.

[1] Goddard, *J. Chem. Soc.*, **123**, 1168 ; 1923.