PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
Volume 19 August 15, 1933 Number 8

THE PHOTOCHEMICAL PRODUCTION OF TRIPHENYLMETHYL

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Communicated June 26, 1933

Triphenylmethyl peroxide is obtained when a cyclohexane solution of triphenylbromomethane, in contact with air or oxygen, is exposed for several hours to sunlight or light in the near ultra-violet region of the spectrum. From the experimental results it appears highly probable that the free radical, triphenylmethyl, is first formed by photochemical dissociation of triphenylbromomethane, and that it subsequently reacts with oxygen to form the peroxide,

$$(C_6H_5)_3CBr \longrightarrow (C_6H_5)_3C + Br \qquad (1)$$

$$2(C_6H_5)_3C + O_2 \longrightarrow (C_6H_5)_3COOC(C_6H_5)_3. \qquad (2)$$

The close relationship between the peroxide which is obtained and the free radical which is postulated gives this reaction a position of particular interest among photochemical processes for which free radical formation has been assumed.

The first evidence of reaction in the radiated solution is the development of a yellow color. The color is not due to triphenylbromomethane since a freshly prepared cyclohexane solution of this substance absorbs only light of wave-lengths shorter than 3800 Å (Fig. 1). The absorption spectrum of the yellow solution shows that at least one of the substances produced by the photochemical reaction absorbs light between 3900 and 5000 Å, a region in which strong absorption bands are found for solutions of either triphenylmethyl or bromine, the products postulated in equation 1.

Since, in the case of the cyclohexane solutions, a considerable yield of the peroxide is produced only after four to ten days of strong illumination, the process is photochemically extremely inefficient. The low quantum efficiency may be attributed to (1) activation of triphenylbromomethane preceding or accompanying Reaction 1, so that only a small part of the radiant energy produces dissociation, or (2) recombination of triphenylmethyl with bromine at a rate sufficiently rapid to prevent the accumulation of any considerable concentration of the free radical. From our experiments dealing with the effect of varying the oxygen pressure, it is probable that the rate is dependent upon a combination of the two effects, with the first predominating.

In each of several test tubes containing a solution of 0.5 g. of triphenylbromomethane in ten cc. of cyclohexane, under constant illumination, and with oxygen available by diffusion as air, crystals were first observed after nine to eleven hours. If this initial period is assumed to be the time required for the concentration of the peroxide to reach a value equal to or slightly greater than the solubility, the total peroxide, as crystals and dissolved material, is approximately proportional to the total time of illumination. Obviously this rate cannot continue throughout the entire

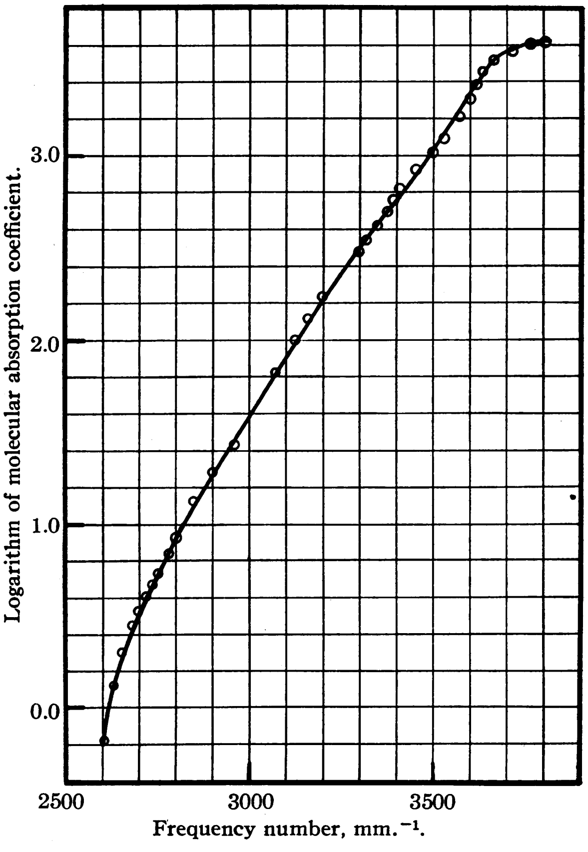

FIGURE 1

Absorption spectrum of solution of triphenylbromomethane in cyclohexane.

reaction, and a rapid decrease will of necessity be encountered during the later stages. The results are in agreement with equation 3:

$$\frac{dP}{dt} = kI\,(1 - e^{-\alpha(R\text{Br})}) \tag{3}$$

in which the rate of formation of the peroxide is directly proportional to the rate of absorption of light by triphenylbromomethane. I is the light intensity, (RBr) is the concentration of the bromide and α is a constant which depends upon the absorption coefficient of the bromide and the dimensions of the reaction tube. According to equation 3, the velocity of reaction should vary with the intensity of the incident light. This point was verified by a series of experiments in which bromine filters were interposed between the light source and the reaction tubes. The dependence of the rate upon the concentration of triphenylbromomethane was checked by comparing the results obtained with different initial concentrations.

The formation of the peroxide is accompanied by other oxidation reactions and the proportion of the oxygen consumed by the side reactions is greater at a higher oxygen partial pressure, but is decreased slightly by circulating the gas through the solution. The yield of the peroxide is also sensitive to these factors. We conclude that the velocity of peroxide formation is controlled by the rate of absorption of light by triphenylbromomethane, and is affected by the partial pressure of oxygen and the rate of stirring of the gas into the solution. Equation 3 is probably the restricted form, for constant oxygen pressure, of a more general relation of the type applied by Bates and Spence[1] to the photoöxidation of methyl iodide. For the photoöxidation of triphenylbromomethane, the equation takes the form:

$$\frac{dP}{dt} = \frac{kI(1 - e^{-\alpha(R\text{Br})})(\text{O}_2)}{k_2(\text{Br}_2) + k_3\,(\text{O}_2)}. \tag{4}$$

The symbols (O_2) and (Br_2) represent the concentrations of oxygen and bromine, and the term $k_2(\text{Br}_2)$ is a measure of the rate of recombination of bromine and triphenylmethyl to form triphenylbromomethane. The appearance of the oxygen concentration in both numerator and denominator is consistent with the relatively small effect that a change in the oxygen pressure has on the rate of formation of the peroxide. The relation between the oxygen concentration in the solution and the pressure in the gas phase is obscured by the probability that the rate of diffusion of the gas into the solution may be an important factor.

Examination of the products formed during eight days of exposure from a solution containing five grams of triphenylbromomethane per hundred cc. of cyclohexane indicated that forty-five per cent of the bromide was converted to the peroxide, twenty-five per cent remained unchanged and thirty per cent could not be accounted for. A small amount of a high-boiling liquid, which contained halogen and possessed phenolic properties, was recovered. This latter substance, not yet identified, is our only clue to the manner in which the bromine produced by photo-dissociation is removed from the solution.

The light source used in the experiments was a Pyrex mercury arc, 16 mm. in diameter, operated at 3 amperes. The solutions were placed in 16-mm. Pyrex test tubes, at a distance of 15 cm. from the lamp. The absorption spectra of the solutions, before and after radiation, were obtained with a Hilger Judd-Lewis sector photometer and Hilger quartz spectrograph, using a high frequency discharge between tungsten electrodes under water as the light source.[2]

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[1] Bates and Spence, *J. A. C. S.*, **53**, 1689 (1931).

[2] Anderson and Gomberg, *Ibid.*, **50**, 203 (1928).

AN AMYNODONT SKULL FROM THE SESPE DEPOSITS, CALIFORNIA

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Communicated July 8, 1933

The Perissodactyla known to occur in the Sespe deposits, north of the Simi Valley, California, include representatives of the Brontotheriidæ and Rhinocerotoidea. The Equidæ remain as yet absent from the record. Within the rhinocerotid division are at present recognized members of both the cursorial and aquatic groups. The collections include a fairly large number of specimens belonging to the Amynodontidæ, among which is the fine skull here described.

Amynodontopsis bodei, n. gen. and n. sp.

Type Specimen.—Skull with cheek-tooth Series $P\underline{3}$-$M\underline{3}$, No. 1087 C. I. T. Vert. Pale., figure 1.

Locality.—Sespe Upper Eocene, north of Simi Valley, Ventura County, California; Locality 150 C. I. T. Vert. Pale.

Generic and Specific Characters.—Larger than *Amynodon antiquus*, *A. advenus* and *A. erectus*, but less robust than *A. intermedius*. Skull dolichocephalic. Nasals short, with anterior ends situated considerably behind level of anterior ends of premaxillaries. Facial fossae extend well back-