

COMMUNICATIONS TO THE EDITOR

X-RAY INVESTIGATIONS ON RUBBER

Sir:

During some earlier x-ray investigations on crêpe rubber, it was observed that the originally translucent sample became more and more milky at the spot where the x-rays passed the material. The sample was the same as described in an earlier paper.¹ This rubber gave a distinct x-ray pattern during the first exposure, but, although the lines did not change their position, they became increasingly sharper with each exposure; simultaneously the opaqueness of the milky spot increased. The increase of sharpness of the originally broad lines represents, of course, increase in particle size; but evidently also the increasing cloudiness of the crêpe rubber shows progressing crystallization.

Another sample of the crêpe rubber was placed in front of the window of the x-ray tube and again slowly the milky spot formed becoming eventually entirely opaque toward transmitted light. The spot obtained was sharply defined by the transmitted x-ray beam and showed no diffuseness at the circumference. After four years of storage, no further changes occurred in the sample. Upon slight warming the milky spot would melt away again.

An increase in the rate of crystallization of gutta-percha, but not of rubber, by means of ultraviolet light was observed by Kirchhof.²

Evidently the above sample of rubber behaves similarly under the influence of x-rays as does gutta-percha with ultraviolet light.

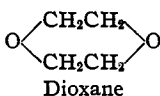
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EMIL OTT

 THE RAMAN SPECTRUM OF DIOXANE

Sir:

During the course of an investigation of the Raman spectrum of some synthetic resins, the solvent dioxane was used. As the spectrum of the latter has not been published previously, I wish to report here my findings.



An apparatus designed by Reynolds and Benford [*Review of Scientific Instruments*, 1, 413-416 (1930)] was used, modified by having a chromium elliptical reflector instead of a silver one, and its major axis in a horizontal rather than a vertical plane. A mercury arc gave the exciting spectrum, exposures of about six hours being made.

¹ E. Ott, *Naturwissenschaften*, 14, 320 (1926).

² Kirchhof, *Kautschuk*, 4, 254 (1928); *C. A.*, 23, 1525 (1929).

The reciprocals of the wave lengths of the modified lines were as follows (the intensities are given in parentheses) and are accurate probably to within 6 cm.^{-1} .

24426 (0), 225 (0), 23878 (4), 691 (3), 590 (1), 496 (1), 408 (2), 267 (2), 22507 (00), 422 (0), 099 (4), 21997 (00), 930 (1), 853 (3), 744 (5), 21640 (1), 556 (0), 501 (1), 20214 (00), 088 (4), 19972 (5). The lines were correlated, respectively, as follows, the ordinal numbers in the preceding list being given first, followed by the respective wave number shift.

Exciting line				23047		Average $\Delta\tilde{\nu}$	
24710		24522		22941			
1	284 (0)	2	297 (0)	9?	434 (00)		291 (0) cm.^{-1}
3	838 (4)	4	831 (3)	10?	519 (0)		837 (4)
5	1120 (1)	7	1114 (2)	11	842 (4)	13	1117 (1)
6	1214 (1)						1214 (1)
8	1443 (2)			18	1440 (1)		1442 (2)
12?	2713 (00)			19	2727 (00)		2720 (00)
14	2866 (3)	16	2882 (1)	20	2853 (4)		2864 (3)
15	2966 (5)	17	2966 (0)	21	2969 (5)		2967 (3)
							434 (00)?
							519 (0)?

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D. S. VILLARS

THE PHOTOCHEMICAL POLYMERIZATION OF ACETYLENE

Sir:

It has been reported by several observers¹ that the polymerization of acetylene to a solid resembling cuprene is induced by either activated mercury atoms or by the direct absorption of ultraviolet light. A quantitative investigation of the photochemical reaction has been undertaken in the hope of throwing some light on the kinetics of the process and to determine whether there is any simple relation between the *quantum yield* and the *ion pair yield* of the analogous radiochemical reaction.²

The following are some of the more important results of this investigation. Using the complete radiation of a quartz mercury arc and a reaction vessel three centimeters deep, the reaction velocity was observed to be proportional to the pressure of acetylene as long as this pressure was not greater than 30 cm.; at higher pressures the velocity approached a constant value. It seems probable therefore that the rate of polymerization

¹ Berthelot and Gaudechon, *Compt. rend.*, 150, 1169 (1910); Bates and Taylor, *THIS JOURNAL*, 49, 2437 (1927); Reinike, *Z. angew. Chem.*, 41, 1144 (1928).

² Lind, Bardwell and Perry, *THIS JOURNAL*, 48, 1556-1575 (1926); Mund and Koch, *Bull. soc. chim. Belg.*, 34, 241-255 (1925).

is proportional to the intensity of the absorbed light but is otherwise independent of the acetylene pressure. Using the same light source, the temperature coefficient of the reaction was determined by comparing the rate at 12 and at 39°. The ten degree temperature coefficient, so determined, has a value of 1.25. It is quite possible that this observed value may be largely the temperature coefficient of the light absorption rather than that of the chemical reaction. Experiments performed with light filters indicate that light of wave length 2537 Å. and longer is not efficient in producing the reaction; this is probably due to the comparative transparency of acetylene in this region.

Several determinations of the quantum yield have been made. The light source used in these experiments was a mercury arc combined with a focal isolation apparatus, which excluded all radiation of wave length greater than 2537 Å. A weighted average of $M/h\nu$, for three separate determinations, is 7.4 ± 2.5 . The uncertainty of this value is due to the precipitation of cuprene on the walls of the reaction cell, which limited the measurements to the first two millimeters' reduction in pressure. These experiments will be repeated with a more sensitive manometer in order to obtain a more accurate value for the quantum yield. Similar experiments with allene and the homologs of acetylene are now in progress. In all experiments a "hot" mercury arc was used, pressures were measured with a quartz spiral manometer and liquid-air traps and gold foil were used to prevent the access of mercury vapor to the reaction system.

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NEW BOOKS

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. Beryllium. System-number 26. Issued by the Deutsche Chemische Gesellschaft, Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1930. xviii + 180 pp. 10 figs. 17 × 25 cm. Price, to subscribers, M. 23.50; singly, M. 30.

This volume covers the history of our knowledge of Beryllium, its occurrence, the preparation and properties of the free element and the preparation and properties of its compounds with elements having system-numbers smaller than 26, namely, the non-metals and the alkali metals. The literature has been covered to May 1, 1930.

The collaborators in the preparation of this volume were Martin Hosenfeld, Hellmut Fischer, Sibylle Cohn-Tolksdorf (atomic and optical properties) and Adrienne Eisner (the complex compounds).