178. *Chemical Action of Ionizing Radiations in Solution. Part XV.* Effect of Molecular Oxygen in the Irradiation of Aqueous Benzene Solutions with X-Rays.*

By M. Daniels, G. Scholes, and J. Weiss.

The chemical effects of *X*-rays (200 kv) on aqueous benzene have been investigated further with particular reference to the nature of the products (in addition to phenol) formed in the presence of dissolved molecular oxygen. Under these conditions, small amounts of an aldehyde, probably mucondialdehyde, are produced; it is suggested that this is produced *via* the intermediary formation of organic peroxy-radicals.

The chemical effects of *X*-rays on aqueous benzene were first investigated by Stein and Weiss,[1] who showed that phenol and diphenyl were the major products formed in the absence of oxygen. Using mixed neutron–γ-ray radiation from radioberyllium and also α-radiation from radon, they found [2] that, *in vacuo*, in addition to the above products obtained by irradiation with *X*-rays, there were formed polyphenols (quinol and catechol) and, in particular, an aldehyde, possibly of a mixture of mucondialdehyde and its partly or fully hydrogenated derivatives. It was thus supposed, in the first instance, that the formation of these additional products by densely ionizing radiations was possibly the result of multiple interactions caused by the high local concentration of radicals. In a later publication the same authors,[3] using a source giving predominantly γ-radiation, reported that oxygen enhanced the yield of aldehyde. Thus it seemed possible that ring fission was connected with the presence of oxygen in solution rather than with high radical concentrations, as it is well known [4] that oxygen is formed in aqueous systems irradiated with more densely ionizing radiations [neutrons (recoil protons), α-rays, etc.]. In view of these observations, we have investigated further the effects of 200-kv *X*-rays on aqueous benzene solutions containing oxygen, particularly with respect to more complex chemical changes in the benzene nucleus.

For these experiments, neutral aqueous benzene solutions were saturated with oxygen and irradiated with doses of the order of 8×10^{-4} ev/N per ml.

Lack of turbidity on irradiation was taken as an indication of the absence of any significant amounts of diphenyl. Indeed, only traces of this substance were detectable in concentrated ether extracts of the irradiated solutions.

A yellow colour formed on addition of alkali to the irradiated solution was discharged

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* Part XIV, *J.*, 1955, 2594.

[1] Stein and Weiss, *J.*, 1949, 3245.

[2] *Idem, ibid.*, p. 3254.

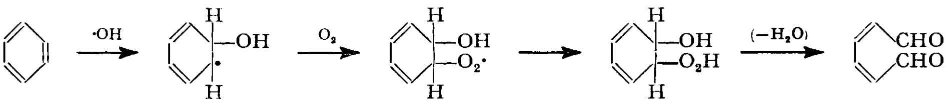
[3] *Idem, ibid.*, 1951, 3265.

[4] Bonet-Maury, *Compt. rend.*, 1948, **226**, 1363, 1445.

by acid. A faint " acid-Folin " reaction for polyphenols[3] was exhibited, and traces of catechol and quinol were detected by paper chromatographic analysis (Riley's method [5]). On reduction of the irradiated solution with sulphur dioxide before analysis, a slight increase in the amounts of detectable quinol was observed and this presumably indicated the formation of some *p*-benzoquinone. The yields of these products were, however, very low, $G \sim 0{\cdot}1$ (molecules/100 ev), and therefore could contribute only relatively little to the overall material balance.

On addition of 2 : 4-dinitrophenylhydrazine to the irradiated benzene solution, an orange-red precipitate was readily formed. This was observed in solutions irradiated with doses as low as $1{\cdot}25 \times 10^{-6}$ ev/N per ml. and thus appeared to be derived from a primary product of irradiation. This hydrazone gave a violet-blue colour with alcoholic sodium hydroxide and was in many respects identical with the corresponding product obtained in Stein and Weiss's neutron irradiations; similarly, a *p*-nitrophenylhydrazone was obtained. We have been unable to prove unequivocally that mucondialdehyde is, in fact, the radiation product responsible for hydrazone formation : of the various substances examined, however, this dialdehyde fits the experimental observations most closely (*q.v.*). The yield was relatively small; estimated from the weight of the bishydrazones, this corresponded to a value of the order of $G \sim 0{\cdot}2$.

When aqueous solutions were irradiated *in vacuo*, on the other hand, no reaction with 2 : 4-dinitro- or *p*-nitro-phenylhydrazine was observed. This suggests that the more complex chemical changes are intimately connected with the participation of molecular oxygen in the radical processes and it is not unlikely that this may be due to the formation, in the first instance, of organic peroxy-radicals leading to a hydroperoxide from which water can be eliminated to give the dialdehyde :



A somewhat parallel case has been observed in the irradiation of aqueous solutions of tryptophan;[6] here it has been shown that opening of the indole ring occurs with the formation of formylkynurenine and that the presence of molecular oxygen in solution is essential.

It is confirmed that phenol is the major product ($G = 2{\cdot}2$) in the irradiation, with *X*-rays, of aqueous benzene containing oxygen; nevertheless, any interpretation of the radiation-induced oxidation should take into account these other chemical transformations.

EXPERIMENTAL

Irradiations.—Solutions were irradiated with unfiltered *X*-rays generated by a Victor Maximar therapy tube operating at 200 kv and 15 mA, by the technique previously described.[7] The dose rate was $3{\cdot}3 \times 10^{-7}$ ev/N per ml., $G_{Fe^{3+}}$ being taken as 15·5. Saturated solutions of benzene were prepared from " AnalaR " grade benzene and triply distilled water; these were then saturated with oxygen.

Nitrophenylhydrazone Derivatives.—The appropriate reagent was added to the irradiated solution and the mixture set aside until precipitation was complete (24 hr.). The precipitates were centrifuged off, washed, dried, dissolved in petrol-benzene (50 : 50, v/v), and chromatographed on acid-washed alumina. The eluting solvents were graded through the series petrol–benzene, benzene, and benzene–ether. The absorption spectrum of each eluate fraction was determined in spectroscopically pure ethanol by use of a " Unicam " spectrophotometer.

With dinitrophenylhydrazones, this method yielded one main and three subsidiary bands. Fig. 1(*a*) shows the visible spectrum of the major component, exhibiting two maxima; on very slow chromatography, a partial (though still poor) resolution was obtained, showing the major component to be a mixture of two closely related substances having maxima at 400 and 450 mμ, severally. Fig. 1, in addition, gives the spectrum of mucondialdehyde bis-2 : 4-dinitrophenylhydrazone (prepared from authentic mucondialdehyde kindly supplied by Professor F. G.

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[5] Riley, *J. Amer. Chem. Soc.*, 1950, **72**, 5782.
[6] Jayson, Scholes, and Weiss, *Biochem. J.*, 1954, **57**, 386.
[7] Farmer, Stein, and Weiss, *J.*, 1949, 3241.

Fischer) and also that of the corresponding derivative of *p*-benzoquinone, both of which were purified by the above chromatographic procedure; resemblance between the spectra of these last two compounds and that of the first component of the radiation product is apparent. On the other hand, the possibility of the presence of *o*-benzoquinone was eliminated by the vast difference in absorption spectra of its dinitrophenylhydrazone from that of the radiation product. Similar experiments likewise eliminated 2-phenylbenzoquinone and diphenoquinone.

Chromatography of the *p*-nitrophenylhydrazone on alumina gave a major band, the spectrum of which is given in Fig. 2(*a*). Here, in contrast to that of the dinitro-compound, only one peak was observed, this being at 445 mμ. Spectra (*b*) and (*c*) in Fig. 2 are those of the mononitrophenylhydrazones of mucondialdehyde and *p*-benzoquinone, respectively. In this case, the spectrum of the *p*-benzoquinone derivative (max. = 380 mμ) differs significantly from that of the derivative obtained from the irradiated solution. The main band of the irradiation product yielded some crystals, m. p. 265° (Fischer and Löwenberg[8] give 264° for the m. p. of mucondialdehyde bis-*p*-nitrophenylhydrazone).

FIG. 1. *Absorption spectra in ethyl alcohol of the* 2 : 4-*dinitrophenylhydrazine derivatives of*: (*a*) Irradiation product. (*b*) Mucondialdehyde (bis-2 : 4-dinitrophenylhydrazone). (*c*) *p*-Benzoquinone (*i.e.*, 4-hydroxy-2′ : 4′-dinitroazobenzene).

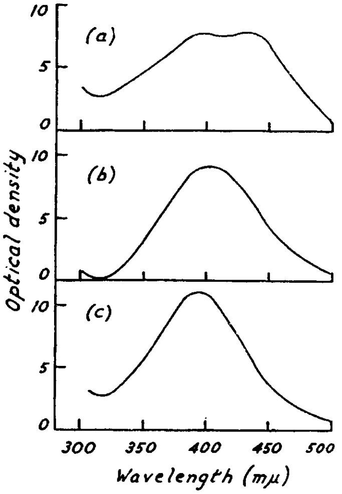
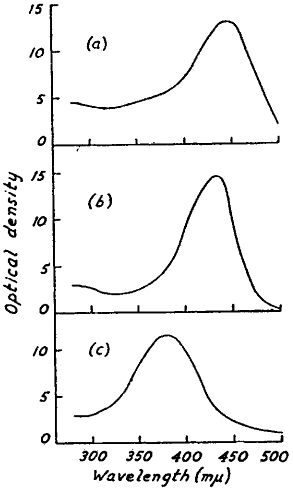


FIG. 2. *Absorption spectra in ethyl alcohol of the* p-*nitrophenylhydrazine derivatives of*: (*a*) Irradiation product. (*b*) Mucondialdehyde (bis-*p*-nitrophenylhydrazone). (*c*) *p*-Benzoquinone (*i.e.*, 4-hydroxy-4′-nitroazobenzene).



Colour reactions of hydrazones with alcoholic sodium hydroxide.

	Irradiation product (main band)	Mucondialdehyde	*p*-Benzoquinone	*o*-Benzoquinone
2 : 4-Dinitrophenylhydrazone	Deep violet-blue	Deep violet-blue	Red-purple	Pale blue
p-Nitrophenylhydrazone ...	Cornflower-blue	Cornflower-blue	Red	Purple

Thus, of the various substances investigated, mucondialdehyde resembles most closely the radiation product, and colour reactions of the various hydrazones with alcoholic sodium hydroxide (see Table) support this deduction. The incomplete correspondence in the spectra may well be of stereochemical origin; it was unlikely that the synthetic sample (of unknown configuration) would necessarily be identical with that produced by irradiation of the benzene solutions.

Elementary analyses of the hydrazone fractions obtained by chromatography did not give satisfactory, reproducible results, the quantities available being too small.

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KING'S COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE UPON TYNE.

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[8] Fischer and Löwenberg, *Ber.*, 1933, **66**, 665.