

ESR-signal. Some systems, however, exhibited an ESR-signal detectable even after that the irradiated samples had been kept in the dark overnight. The maximum spin concentration indicated that about 0.1 % of the acceptor molecules had been transformed to paramagnetic centres.

The ESR-spectra recorded during light excitation exhibit a hyperfine structure which can be more or less definitely correlated with a free radical derived from the acceptor part of the EDA-complexes. Fig. 2b shows the light-induced ESR-spectrum of *s*-trinitrobenzene dissolved in tetrahydrofuran. Due to the high symmetry of the molecule the three nitrogen nuclei produce a common splitting into three main lines separated by 13 gauss. Each of these lines is split into a quartet of equally spaced lines (3.0 gauss) by the three hydrogen atoms with the intensity ratio of 1:3:3:1. The appearance of this spectrum did not change even after irradiation for several hours. When dissolved in dimethoxyethane, however, a further splitting of the spectrum initially identical with that obtained in tetrahydrofuran was observed after prolonged irradiation.

The spectral distribution of the energy from light source (A) is well outside the absorption of tetrahydrofuran without any solute, and involves only a rather weak absorption in the solutions here investigated, whereas source (B) emits radiation in a region of relatively high absorption as concerns both the solvent and the solutions. Comparing the results obtained for the systems tetrahydrofuran — chloranil and tetrahydrofuran — *s*-trinitrobenzene by use of (A) and (B) respectively, however, no qualitative differences could be detected.

Discussion. It is believed that a charge transfer which unpairs the electrons involved is produced by the absorption of radiant energy. The subsequent reactions of the paramagnetic complex, a triplet state or, more probable, a biradical may take different paths. The excited chloranil complexes seem to return to the initial state without any dissociation into radical ions as judged from the relatively rapid decay rates and their apparent independence of the temperature. On the other hand the photo-activated complexes involving the nitro substituted derivatives of benzene are dissociated into radical ions as evidenced by their temperature dependent decay rates. The hyperfine structure of the *s*-trinitrobenzene spectrum is consistent with the formation of negative free radical ions by

a transfer of one electron without any transfer of hydrogen atoms. In other systems the radical ions formed evidently partake in secondary reactions.

Evidence for positive radical ions derived from the donor part of the EDA-complexes seems to be lacking. A hypothetical explanation may involve a very short life time of these radicals.

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Enrichment of Light Isotopes of Sulphur, Carbon and Oxygen Using an Anion Exchanger

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It is known that upon displacement of hydrogensulphite ions from an anion exchanger by a strong acid there is an enrichment of heavy sulphur isotopes at the boundary formed¹. Similarly it is to be expected that upon absorption of sulphur dioxide from a solution on an anion exchanger column in the acetate ion form there will be an enrichment of the light sulphur isotope at the boundary formed. Several experiments have confirmed this. In the following only one is described.

In the experiment the 7 columns used were of 12 mm inner diameter and about 140 cm length, filled with Dowex 2-x10, 100–200 mesh, acetate ion form. They were connected in series by narrow glass tubes (2 mm inner diameter). On the columns there were absorbed a number of samples of SO₂, pre-enriched in ³²S by ion exchange, until there had formed a band of 255 cm length, visible by its yellow color.

Table 1. Data and analysis of samples of SO₂ from anion exchanger experiment. Travelled length 116.5 m during 43 days at room temperature.

Sample No.	Volume ml	Band length cm	C _{SO₂} mole/l	g SO ₂	Q ³⁴ / ₃₂
1	2	—	—	—	0.0634
2	75	13	0.343	1.65	0.071
3	100	23	0.355	2.27	0.121
4	200	46.5	0.413	5.28	0.185
5	200	52.5	0.385	4.92	0.267
6	200	39	0.440	5.63	0.347
7	170	37	0.400	4.35	0.704
8	2	—	—	—	1.29
Sum	949	210		24.10	

Table 2. Acetic acid samples from an anion exchanger after 31 m displacement.

Sample No.	Volume ml	Band length cm	C _{CH₃COOH} mole/l	Q ¹³ C	Q ¹⁸ O
1	88	23	0.56	1.00	1.00
3	113	32	0.536	0.997	0.985
3	78	24	0.514	0.912	0.754
4	73	19	0.434	0.778	0.561

The band was displaced with 0.3 M HCl and when leaving the last tube it was returned to the first one, which meanwhile had been regenerated and washed. After 66 meter travel the band had shrunk to 211 cm, probably chiefly due to losses from the back boundary. More SO₂ was added at the middle of the band until its length was 245 cm. The displacement was continued and when the band had travelled a total of 116.5 m it had again shrunk to a length of 212 cm. Then all of the band was taken out as eight samples which were investigated for isotope abundance. For data see Table 1, where *Q* is the relative abundance of ³⁴S in the sample compared with its natural relative abundance.

If the elementary separation factor is assumed to be $\alpha_{34/32} = 1.0064$, as was found in one experiment, the total separation factor between the ends of the band (20.3) corresponds to 471 theoretical plates. However, completely stationary conditions had probably not been reached.

An isotope enrichment may also be expected on exchange between acetic acid and acetate ion. In order to investigate this, four samples of the acetic acid effluent in front of the sulphurous band were taken after 31 m travel. The acetic acid was transformed to barium acetate. This was pyrolyzed to barium carbonate, which

was decomposed with concentrated sulphuric acid to given carbon dioxide for isotopic analysis. In this way the carbon and oxygen isotope content of the acetic acid carboxyl was obtained. The results are given in Table 2.

The high concentration of the acetic acid in the effluent indicates that it is partly bound to the ion exchanger as unionized molecules or single-ionized double molecules. The acetic acid concentration in the effluent is variable and no exact proportionality is found between sample volume and band displacement length. For these reasons no exact calculation of elementary separation factors can be made. However, a conservative estimate shows that upon exchange between acetate ion plus acetic acid on the exchanger and acetic acid in the solution the carboxyl of the acetic acid in the solution is enriched in ¹³C by the elementary factor 1.0016 and in ¹⁸O by the factor 1.0036.

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