plotted together with the extremal energy of protons formed by reaction (2) (dashed line). Data points in this figure represent maximum values of the peak in question, error bars express the uncertainly in assigning their positions. The explanation proposed seems to be confirmed.

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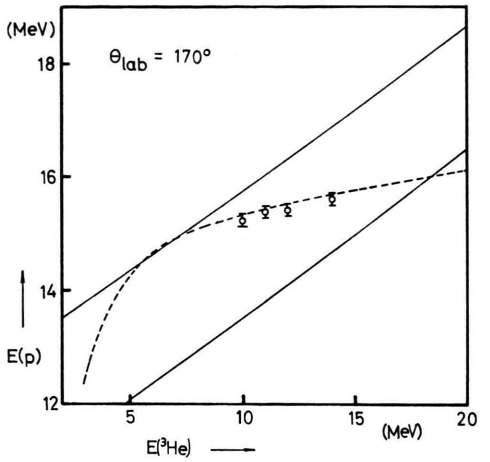

Fig. 5. Energies of protons corresponding to ground and first excited state peak of ^{8}Be (drawn lines) and maximal energy of protons from reaction (2) as functions of the beam energy. Data points represent maximum values of protons formed by reaction (2), taken from spectra shown in Fig. 1 – 4.

Photo-Induced Electron Transfer in Dye-dimethylsulfoxide-metal Ion Complexes: Electron Spin Resonance Investigations

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Dedicated to Professor Dr. W. Gentner *on the occasion of his 60th birthday*

Fluorescence quenching and sensitized photoconduction was observed recently by several investigators in systems containing aromatic amines[1] or sulfhydryl proteins[2] and a fluorescent dye. The mechanism proposed for this effect is based on an electron transfer from the amine or protein to the excited dye molecule. In this communication it will be shown that an electron transfer also occurs during illumination of a methylene blue (MB)-dimethylsulfoxide (DMSO) system. Added metal ions, such as Cu^{2+}, were observed to act competitively with the dye in their electron accepting ability.

The quenching of the fluorescence of the dye by electron transfer has been investigated by electron spin resonance (ESR) technique. A Varian Model V 4500 100 kc ESR spectrometer at a frequency of 9.5 Gc/sec with a liquid sample accessory was used for these studies. The position of the signals was determined with a standard DPPH (diphenylpicrylhydrazil) reference signal for which $g = 2.0036$. All measurements were done at room temperature.

Methylene blue (Allied Chemical and Dye Corp., New York) was dissolved in DMSO (Matheson Scientific, Inc., East Rutherford, N. J.); concentrations used varied from 2.3 to 9.4 mM. In order to study the influence of metal ions on the charge transfer reaction, varying amounts of cupric chloride ranging from 0 to 171.6 μM were added to a 10 mM MB-DMSO solution. These Cu^{2+}-concentrations were too small to produce an ESR signal.

Illumination of the MB-DMSO system with white light resulted in a single line about 8 Gauss wide and located at $g = 2.003$. No signal was obtained when DMSO alone was illuminated. The light-induced ESR signal increased with illumination time as well as with the concentration of MB; it reached a plateau after about 20 to 30 min (see Fig. 1). A possible explanation for the effect observed might be that the excited dye reacts with DMSO transferring an electron from DMSO to the dye. This results in an oxidized DMSO and a reduced dye molecule, leaving, as was observed, the leuco (colorless) form of MB. A negative charge, associated with the oxygen atom as a result of its electronegativity, along with the electron donating effects of the two methyl groups, is probably involved in the electron release. The fact that no signal was observed during illumination of solutions with constant MB-concentration, using water, glycerol, ethanol, acetone or formamide as a solvent, supports this concept. Since acetone and DMSO differ in structure only by the replacement of a carbon atom by a sulfur atom, we might conclude that sulfur is important for this electron release. Furthermore, these results are consistent with a similar electron transfer mechanism for the fluorescence quenching of a dye proposed by Weiss[3] and interpreted later on by Kasha[4] in terms of a collisional perturbation of spin-orbital coupling.

A light-induced oxidation-reduction reaction seems to be involved in the fluorescence quenching effect observed. Since no reduction occurred without ex-

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[1] W. C. Needler, J. Chem. Phys. **42**, 2972 [1965].

[2] E. Fujimori, Nature (London) **201**, 1183 [1964].

[3] J. Weiss and H. Fischgold, Z. physik. Chem. B **32**, 135 [1936].

[4] M. Kasha, J. Chem. Phys. **20**, 71 [1952].

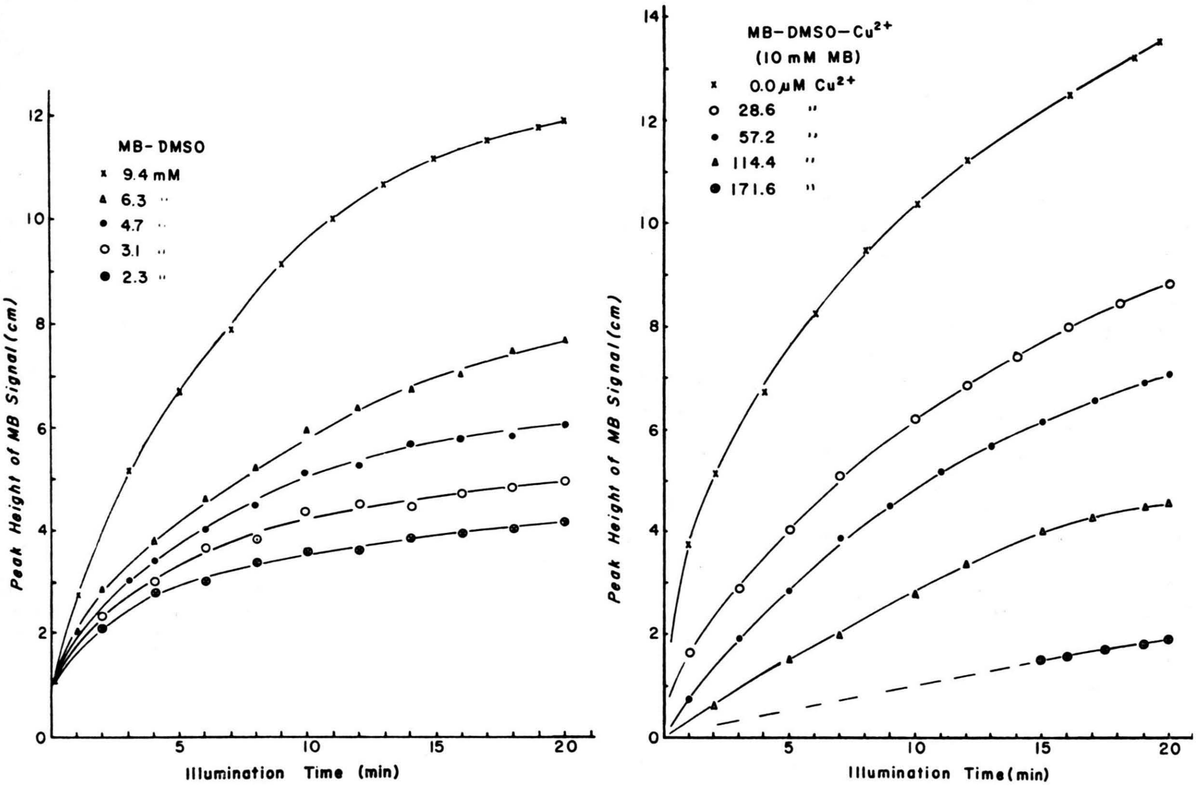

Fig. 1. Effect of illumination on the methylene blue (MB)-dimethylsulfoxide(DMSO)-Cu^{2+} complex.

citation, it must be concluded that the redox potential of the ground state of the dye molecule is lower than that of DMSO. Moreover, the dye is apparently capable of preventing the recombination of the accepted electron with the oxidized DMSO for certain periods of time, which might be due to the electron affinity of the dye: two hours after turning off the light, about 50% of the maximum peak height was still present.

A further indication for the mechanism proposed was obtained when metal ions, especially Cu^{2+}, were added to the MB-DMSO solutions. Illumination with light resulted in the production of the ESR signal mentioned. However, the signal height obtained was inversely proportional to the Cu^{2+}-concentrations used (see Fig. 1). This suggests that the mechanism described above can be applied. However, the electrons released from DMSO migrate to Cu^{2+} rather than to MB. The higher electron affinity of metal ions and their ability to form a complex with DMSO might account for this effect [5]. No complex formation between the sensitizing dye and DMSO could be detected spectrophotometrically.

From the results obtained it might be concluded that, during illumination, the excited dye acts as a sensitizer (catalyst) for electron transfer from DMSO to the dye or to the metal ions when they are present. The ESR signal observed seems to be produced by the electron transferred to MB and which is presumably located at the sulfur atom.

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[5] W. Lohmann, C. F. Fowler, and J. L. Sanders, Nature (London) **209**, 908 [1966].