

Photochemical reactions in alkali halide matrix, decarboxylation of maleic acid into ethylene by uranyl nitrate in a pressed potassium bromide disk

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Abstract—The feasibility of quantitative photochemical reactions of organic compounds in the solid alkali halide disk, usually used for the study of infrared spectroscopy has been explored. The disks were prepared by mixing maleic acid, uranyl nitrate and potassium bromide. Ultraviolet light was used for the irradiation of disk and the products were identified by infrared spectroscopy. It has been observed that the rate of reaction increases with the time of irradiation. The results indicate that the ethylene and uranyl (VI) complex of carboxylate are formed with the decarboxylation of maleic acid, sensitized by uranyl nitrate.

INTRODUCTION

SCHMIDT *et al.* first used potassium bromide for the study of i.r. spectra of solids [1]. Later potassium bromide disks were used for the study of thermal decomposition of peroxide and nitrate esters [5], and photochemical reactions by u.v. and i.r. spectroscopy [6-10].

Only rare observations were found in the literature for the photochemical reaction of organic compounds in pressed alkali halide disk. The pellet technique is very useful for the study of complex organic and labile molecules, which interact with the solvent molecule and choice of an inert solvent is rare. Further, only a nanogram of sample is required in this technique. A thorough survey of literature has shown that no work seems to have been done on the photochemical reactions of maleic acid. Thus the aim of this study was to evaluate intra- and intermolecular photochemical reaction of maleic acid sensitized by uranyl nitrate.

RESULTS AND DISCUSSION

The potassium bromide disks of maleic acid and maleic acid-uranyl nitrate have been irradiated with u.v. light for 10, 20, 30, 45 and 60 min. Infrared spectra were recorded after each irradiation to follow the course of photochemical reaction. The reaction products were identified by measuring the intensity of bands of interest using Gaussian curve analysis method [11] (Table 1).

The infrared spectra of maleic acid and potassium bromide disk after and before irradiation had shown no change in the band intensity and their position. Thus maleic acid itself was photochemically inactive in potassium bromide disk.

The disappearance of bands in the region 3400-2500 cm^{-1} in the maleic acid-uranyl nitrate system indicates decarboxylation of maleic acid. The rapid diminution of the carbonyl band at 1705 cm^{-1} provides confirmatory evidence for the decarboxylation.

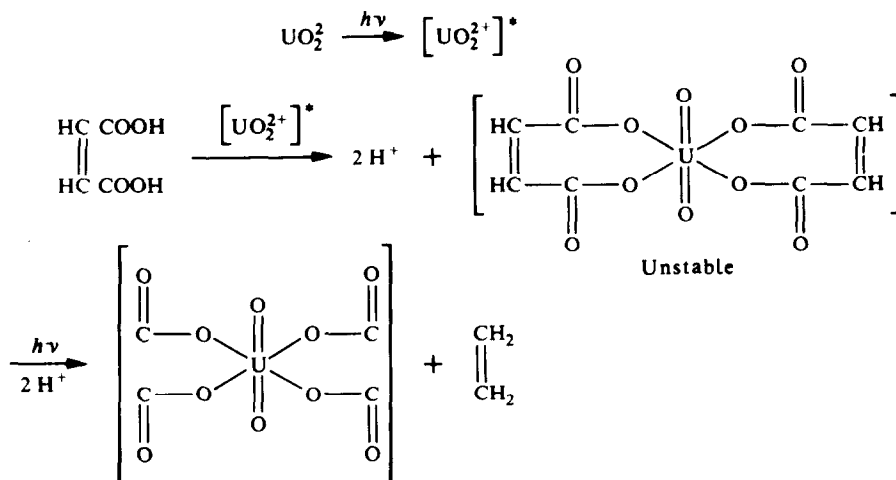


Table 1. Effect of period of irradiation on maleic acid-uranyl nitrate system

Sample in disk	Time of irradiation (min)	Intensity of the band $\times 10^{-5}$ ($l \text{ mol}^{-1} \text{ cm}^{-2}$)							
		1630	1705	1590-1540	1470	1430	1265		
Maleic acid	0	15.97	11.4	15.69	9.0	20.29	10.74	10.52	5.6
		1630-1540						1460-1420	
Maleic acid + uranyl nitrate	0	17.97	11.4	10.98	26.16	9.40	10.52	6.7	
Maleic acid + uranyl nitrate	10	17.97	19.28	10.98	26.16	9.40	12.84	6.7	
Maleic acid + uranyl nitrate	20	19.9	19.28	7.84	29.07	10.52	12.84	7.85	
Maleic acid + uranyl nitrate	30	19.9	19.28	6.27	27.62	10.52	10.04	9.20	
Maleic acid + uranyl nitrate	45	21.96	21.03	6.27	29.02	11.84	10.04	9.20	
Maleic acid + uranyl nitrate	60	21.96	21.03	4.2	31.9	12.12	13.27	10.2	

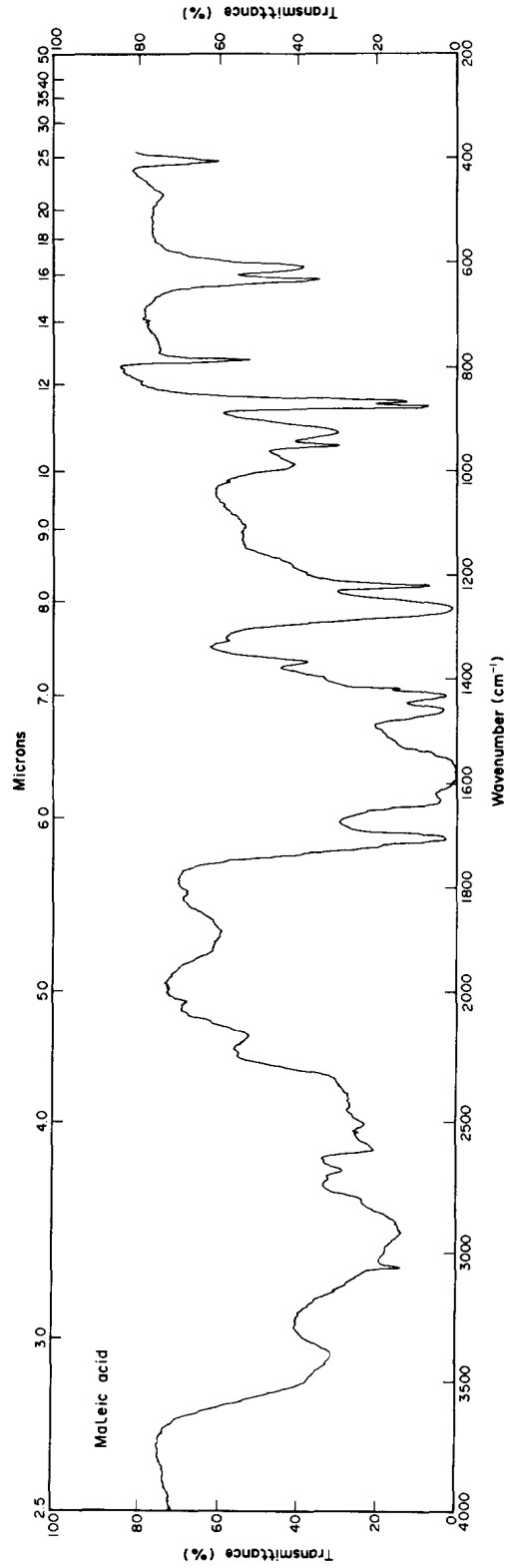


Fig. 1.

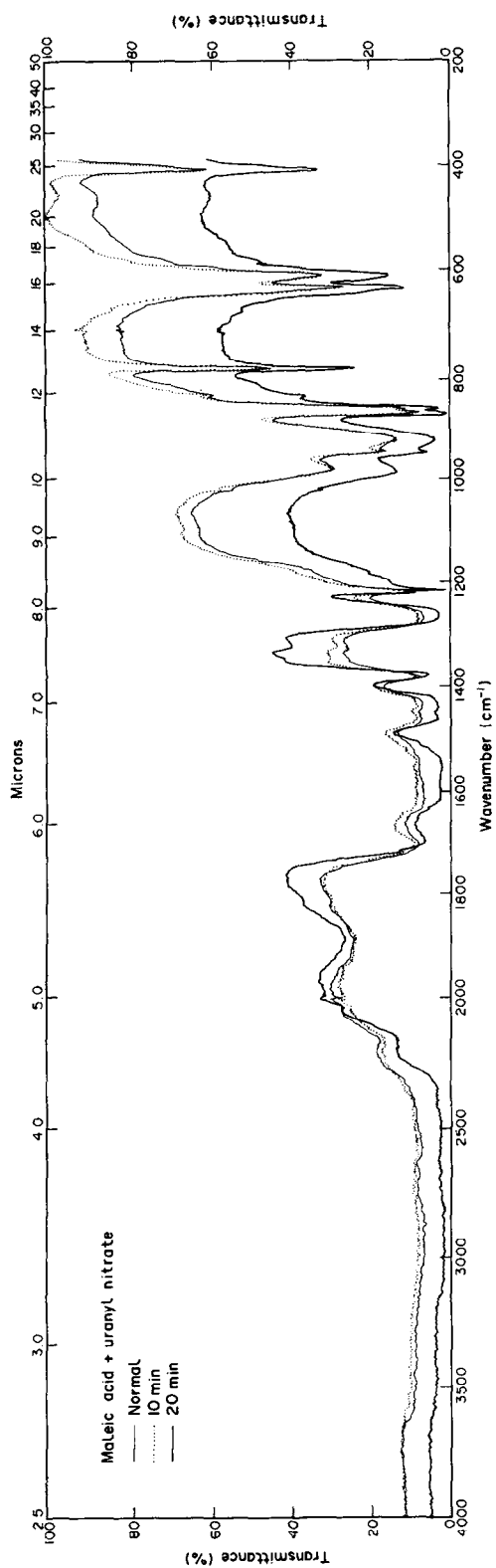


Fig. 2.

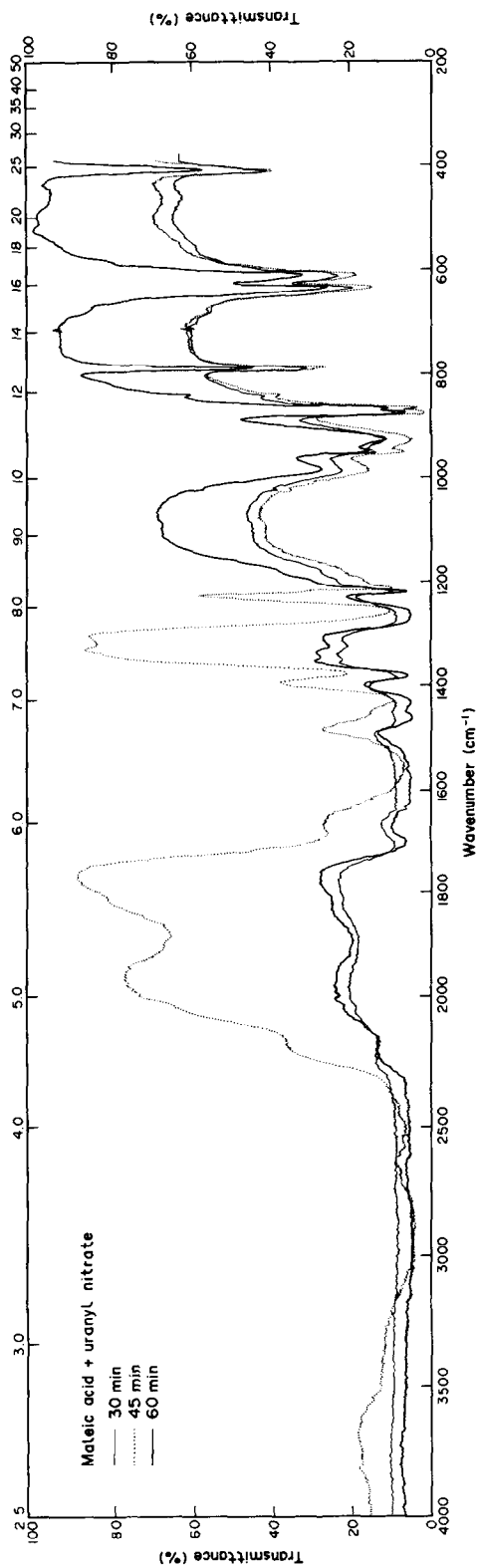


Fig. 3.

Increase in band intensity at 1880cm^{-1} with irradiation time had been thought to indicate the formation of maleic anhydride as a reaction product, but lack of a band in the region $1180\text{--}1035\text{cm}^{-1}$ (C–O–C, Str.) ruled out the formation of maleic anhydride.

The appearance of a broad band in maleic acid–uranyl nitrate system at $1630\text{--}1540\text{cm}^{-1}$, with increasing intensity as the irradiation time was increased, has been assigned to unsaturation (C=C) and symmetric vibration of uranyl (VI) complex of carboxylate. In the same way appearance of a broad band at $1460\text{--}1420\text{cm}^{-1}$ in uranyl nitrate–maleic acid system, ($=\text{CH}_2$ def. *cis* and antisymmetric vibration of uranyl complex of carboxylate) confirms the formation of ethylene and uranyl (VI) complex of carboxylate as photoproducts.

The increase in band intensity at 1930 and 1880cm^{-1} (overtone band)[13] and 1265 and 950cm^{-1} (CH def. in-plane and out-of-plane vibration)[13] with irradiation affords a useful confirmation for the formation of ethylene as photoproduct.

The photochemical action of uranyl ions with organic acids involves, either a direct photochemical oxidation of the reductants with the concomitant reduction of U(VI) to U(IV), or a sensitization for oxidation by other oxidant, particularly molecular oxygen i.e. autooxidation and photosensitized decarboxylation. HECKLER *et al.* [14] have studied the photochemical reaction of dicarboxylic acid in aqueous media and report the formation of carbon dioxide and carbon monoxide as the reaction products. Later BANSAL [15] also found the same products, when he studied the photochemical reaction of organic acids in solid potassium bromide disks.

The mechanism of photochemical reaction of maleic acid–uranyl nitrate system; which is strongly supported by experimental observation involves the oxidation of maleic acid by excited uranyl ion to form sterically unfavourable uranyl (VI) complex of maleic acid by eliminating protons, followed by decomposition of complex to give uranyl (VI) complex of carboxylate and ethylene by proton transfer steps. Actually this process involves the rupture of a C–C bond and the formation of an H–C bond, which requires about 15 Kcal less energy than the reaction in which the H–C bond broke and the H–H bond formed [16], thus the following mechanism was proposed for such a process.

EXPERIMENTAL

Spectroscopic grade potassium bromide was obtained from BDH (India) and used without any treatment. The maleic acid and uranyl nitrate were from BDH, AR grade and used without further purification. The potassium bromide disks were prepared by mixing maleic acid (1 mg) and uranyl nitrate (0.5 mg) with KBr (1 g) in a vibrator and the mixture was pressed under vacuum into disks of 14.5 mm diameter and 1.1 mm thickness under a pressure of 15 tons. To prepare transparent pellet the ratio of KBr and sample were kept reasonably high.

Photochemical reactions were carried out at room temperature by irradiating the KBr pellet with u.v. light. Ultraviolet source used was a u.v. lamp (300 W) with maximum transmission of 41% at 329 nm. The u.v. source was kept at 7.5 cm away from the disk. After irradiation the disk was suspended in the light path of Perkin–Elmer 377 grating Infracord spectrophotometer. The nature of reaction was followed by recording the spectra on the same chart, as a function of time of irradiation. To prevent severe scattering of radiation the disk was recompressed at a pressure of 1/4 of the initial pressure in a die after irradiation.

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