Photoprocesses in maleic acid

V.I. Sachkov and E.I. Sachkova

V.D. Kuznetsov Siberian Physico-Technical Institute, Tomsk

Received February 1, 2000

The most probable mechanisms of photochemical transformations in maleic acid are considered and an attempt is made to explain the much complicated kinetics of these transformations. The absorption spectrum of the maleic acid in the range from 200 to 400 nm was recorded and the molecule has been calculated by the INDO method.

Carboxyl compounds containing C = O group are the most important chromophores in the photochemistry. The main advantage of such compounds is their high thermostability though possessing an increased photochemical activity.

The C = O groups are of prime importance in synthetic polymers, because they play a significant role in the initiation and spread of the photooxidation processes in hydrocarbon polymers exposed to action of natural radiation on the Earth surface. Carboxyl compounds with their conjugated unbound structure attract a particular interest due to their high reactivity under exposure to electromagnetic radiation. Such structures are active in reactions of nucleophilic addition, isomerization, cyclization, chain polymerization, and so on. Maleic acid is an example of such a structure, therefore studying physicochemical and spectral properties of this molecule and other similar molecules is of great scientific interest.

Maleic acid (Fig. 1) is a classical example of photochemical *cis-trans*-isomerization. The *trans*-form of maleic acid – fumaric acid (Fig. 1) – significantly differs from maleic acid by its principal physical characteristics.

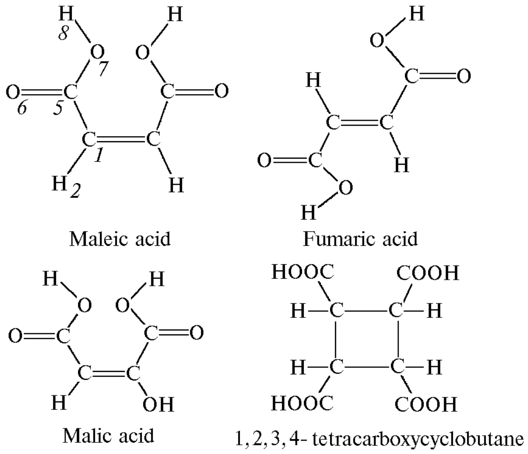
Maleic acid
Fumaric acid
Malic acid
1,2,3,4- tetracarboxycyclobutane

Fig. 1. Structure formulae of maleic acid and its photochemical products.

Table 1. The main physicochemical properties of maleic and fumaric acids

Acids	T_m, K	Solubility in 100 g of H_2O, g	10^5 K′	10^5 K″
maleic	400.5	79	1000	0.055
fumaric	575	0.7	96	4.1

Isomerization of maleic acid under exposure to electromagnetic radiation of mercury lamp is known[1] since the 1930's. The isomerization proceeds both in the direction toward *trans*-isomer formation and backwards. Overcoming the barrier of substituents rotation about C = C bond requires about 2.4 eV energy. This is a classical example of photochemical reaction. Unsensibilized *cis-trans*-isomerization is initiated by radiation within the absorption band of unsaturated compound, and the result of the reaction essentially depends on the absorptance of both isomers. As a rule, the *cis*-isomer absorbs in the region of shorter waves, and its extinction coefficient is lower as compared with the *trans*-isomer. The photochemical processes in such reactions follow the Cauchy law. Inasmuch as in an isomer mixture it is the *trans*-isomer that is primarily the excited component, its concentration decreases under the effect of long exposure. This is accompanied by simultaneous increase in the *cis*-isomers concentration. In some time the proportion between these concentrations comes to a constant value, i.e., to a "photostationary state," as it is called.

Recent development of lasers has opened new possibilities of studying nonlinear photochemistry of organic and bio-molecules in liquid solutions. Thus, in 1980's, a series of new photochemical reactions was discovered, among them a formation of malic acid and 1,2,3,4–tetracarboxycyclobutane under the exposure of the maleic acid in aqueous solution to ultrashort-wave laser radiation (Fig. 1).[2] These transformations follow two-quantum excitation mechanism.

The absorption spectrum of the maleic acid in aqueous solution was determined using automated setup based on the laboratory spectrophotometer SP–26. As the experimental data show (Fig. 2), the maleic acid spectrum is a composite wide band in the wavelength

0235-6880/00/03 265-02 $02.00

range from 200 to 400 nm. As is seen from the spectrum (Fig. 2), $\pi\pi^*$-transition falls into the wavelength range from 200 to 300 nm, whereas the $n\pi^*$-transition – in 300–350 nm range. The recording of the $n\pi^*$-transition is a considerable challenge because it has energy close to that of the $\pi\pi^*$-transition and because of small value of ε.

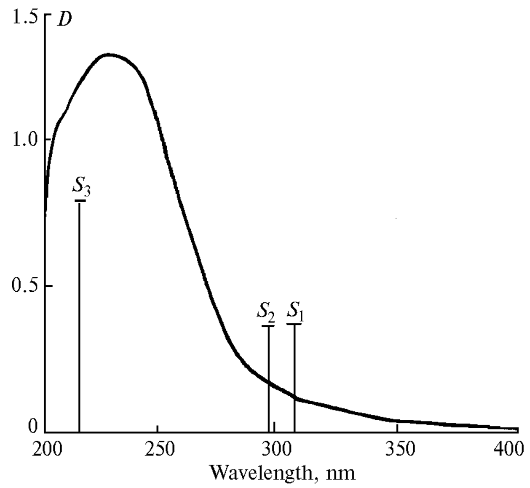

Fig. 2. Absorption spectrum of maleic acid in aqueous solution.

Analysis of atom charges (Table 2) has shown the hydrocarbon atoms of double C = C bond undergo maximum change of charges. The electron density on these atoms decreases, what, possibly, causes the C = C bond weakening favorable for the proceeding of reactions.

Table 2. The charge on atom of the maleic acid molecule in excited states

State	Atom charge, *e*					
	Q_1	Q_2	Q_5	Q_6	Q_7	Q_8
S_0	−0.210	0.039	0.656	−0.635	−0.249	0.210
S_1	−0.168	0.048	0.526	−0.355	−0.262	0.212
S_3	0.070	0.037	0.545	−0.395	−0.267	0.270
T_1	0.090	0.039	0.532	−0.606	−0.265	0.210
T_4	−0.111	0.039	0.466	−0.514	−0.091	0.210

To elucidate the kinetic peculiarities of the reactions and detailed photophysical mechanism of maleic acid transformations, the programmable method based on numerical approximation by differential overlapping was used for calculating the electron transitions. Quantum-mechanical calculation has shown the state S_1 to be a state of $n\pi^*$ type, a transition into which from the fundamental one is characterized by the oscillator strength $f = 10^{-3}$.

As is seen from the diagram of electron states (Fig. 3), the classical photochemistry of the maleic acid proceeds predominantly by the channels $S_1 \rightarrow T_3 \rightarrow \rightarrow S_0$, $S_3 \rightarrow T_4 \rightarrow S_0$, which are tightly connected by spin-orbital mechanism. The computation of intercombination conversion constants and oscillator strengths has proved such photochemistry of maleic acid. The intercombination conversion constant K_{ST} for $S_1 \rightarrow T_3$ equals 10^{10} ($f = 10^{-3}$), for $T_3 \rightarrow S_0$ $K_{ST} = 10^6$, for $S_3 \rightarrow T_4$, $K_{ST} = 10^{11}$ ($f = 0.6$).

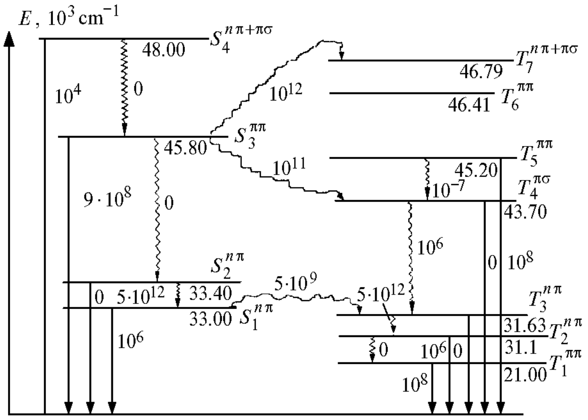

Fig. 3. Diagram of electron transitions in maleic acid molecule.

”y this means we have studied the nature of channels of energy accumulation in the lowest excited states; determined the spectrum of maleic acid; computed the intercombination conversion constants, oscillator strengths, and charge distribution over fundamental and lowest excited states.

Acknowledgments

We are grateful to V.Ya. Artukhov, the Chief of laboratory at the Tomsk State University, who kindly presented at our disposal the package of applied software based on the INDO method.

References

1. A.R. Olson and F.L. Hadson, J. Amer. Chem. Soc. **55**, 145 (1993).
2. E.V. Khoroshilova, N.P. Kuzmina, V.S. Letokhov, and Yu.A. Matveetz, Appl. Phys. B. **31**, 143 (1983).