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THE REACTION OF MALEIC AND PHTHALIC ANHYDRIDES WITH 2-METHYLIMIDAZOLE

Yu. M. Evtushenko, B. E. Zaitsev, V. M. Ivanov, and K. M. Gitis

The reaction of maleic anhydride with 2-methylimidazole in acetonitrile and DMF is accompanied by the appearance of strong absorption bands in the visible part of the spectrum due to the formation of molecular complexes. In acetonitrile the reaction proceeds by two routes via the formation of an amide and the molecular complex. Phthalic anhydride reacts with 2-methylimidazole to give amide but not to form molecular complexes.

Keywords: 2-methylimidazole, N-acyl-2-methylimidazoles, π-complexes, electronic absorption spectra.

Imidazole catalyzes the phthaloylation reaction of alcohols, which is used for the quantitative determination of hydroxyl groups in polymeric materials [1], but the reaction rate in the presence of the imidazole is an order higher than in pyridine. The different catalytic activity of the imidazoles and tertiary amines with relation to the anhydride determined the particular kinetic and stoichiometric features of the reaction process. The aim of our work was to study the chemical nature of the reaction of maleic and phthalic anhydrides with 2-methylimidazole (**1**). These anhydrides were chosen because phthalic anhydride (**2**) is one of the widely used reagents for hydroxyl groups [2] and maleic anhydride (**3**) forms colored compounds in solution with imidazoles.

IR spectroscopy was used to study the initial stage of the reaction of anhydride **3** with 2-methylimidazole **1** in acetonitrile up to the formation of a white precipitate. At the beginning of the reaction of anhydride **3** with imidazole **1** there are present two absorption bands at 1780 and 1800 cm^{-1} (this band is at 1780 cm^{-1} in the spectrum of the starting anhydride **3**) and the intensity of the second band increases with an increase in the concentration of compound **1**. The reaction takes place with a change in the color of the solution from colorless to yellow and then to orange. The latter color change is accompanied by the formation of a precipitate and a decrease in the intensity of both absorption bands, moreover the decrease in the intensity of the band at 1800 cm^{-1} occurs much more rapidly than that at 1780 cm^{-1}. Anhydride **2** reacts with imidazole **1** in acetonitrile much more slowly and without a change in the color of the solution or the formation of a white precipitate. In addition, in the IR spectrum of the solution, the absorption bands at 1800 and 1780 cm^{-1} disappear and are replaced by absorption bands for an acid (1720 cm^{-1}) and an acid amide (1660 cm^{-1}) [3].

The reaction of anhydride **3** with an excess of triethylamine or imidazole **1** in DMF is accompanied by an increase in the band half width for the absorption in the electronic spectrum at 278 nm to the long wavelength region, an appearance of the shoulder in the region 330 nm and low intensity bands in the visible region at 370 and 450 nm, which change the color of the solution (Fig. 1). In the early stage of the reaction between reagents **1** and **3**, the intensity of the absorption band at 450 nm increases sharply and then gradually decreases (similarly to the absorption band at 1800 cm^{-1} in the IR spectrum of the solution in acetonitrile). For a 1:1 ratio of the reagents **1** and **3** the spectrum shows a clearly marked isobestic point at 284 nm which is absent at a ratio of 1:2.

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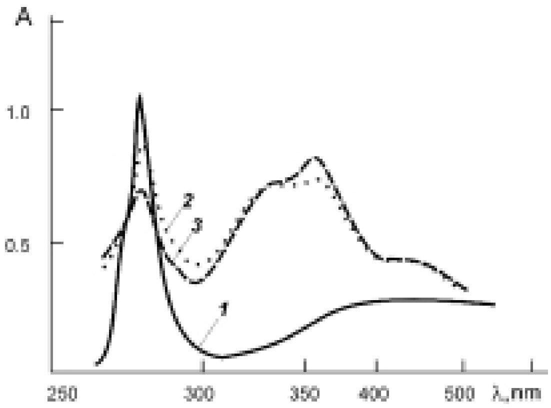


Fig. 1. Electronic spectra of compounds in DMF (*l* = 1 cm):
1 – maleic anhydride (0.037%) + 2-methylimidazole (0.031%), reaction time 1 min;
2 – maleic anhydride (0.037%) + 2-methylimidazole (0.031%), reaction time 90 min;
3 – maleic anhydride (0.037%) + 2-methylimidazole (0.062%), reaction time 90 min.

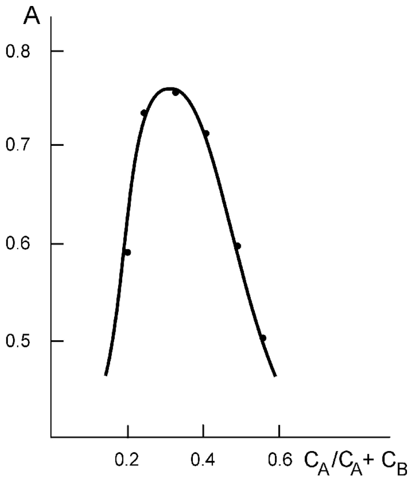


Fig. 2. Isomolar series in DMF (480 nm filter), *l* = 1 cm,
C_A – maleic anhydride;
C_B – 2-methylimidazole.
$C_A + C_B$ = constant = 3.1×10^{-3} molar

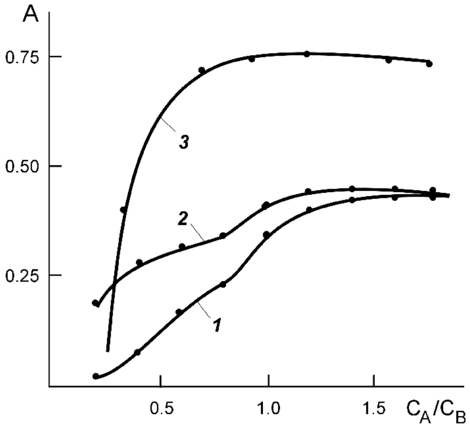


Figure 3. Saturation curves for 2-methylimidazole / maleic anhydride in DMF in optical density coordinates versus concentration (480 nm filter, *l* = 1 cm):
1 – at a constant concentration of 2-methylimidazole (C = 0.061%, reaction time 3 h);
2 – at a constant concentration of 2-methylimidazole (C = 0.061%, reaction time 12 h);
3 – at a constant concentration of maleic anhydride (C = 0.051%, reaction time 3 h).

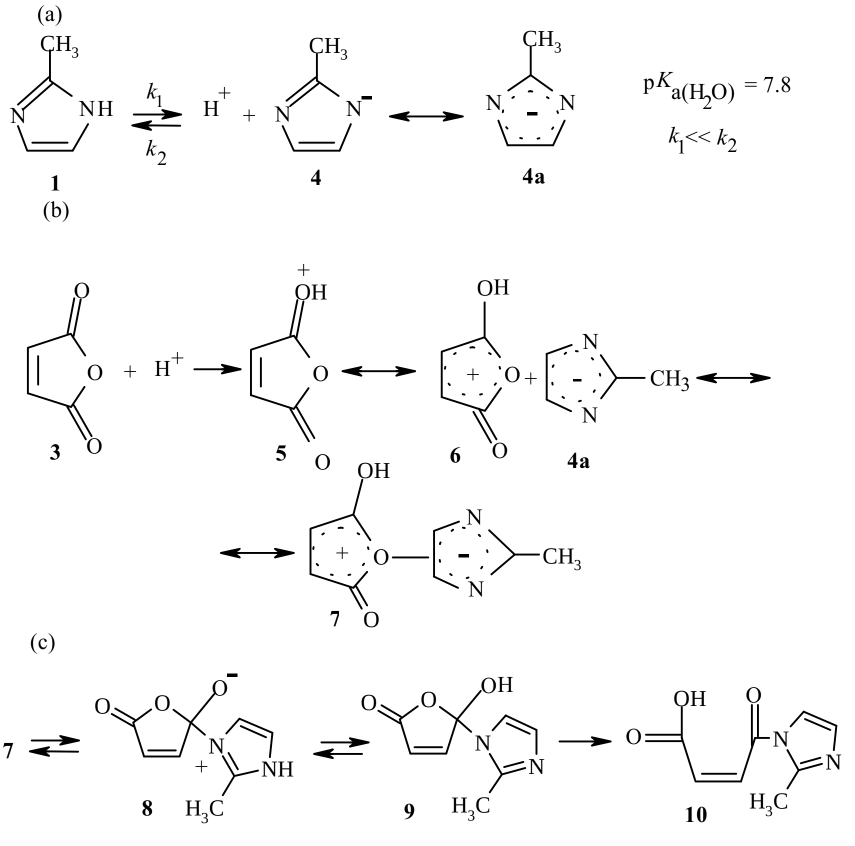
The spectrophotometric methods of isomolar series (Fig. 2) and of saturation (Fig. 3) [4] were used to determine the composition of the formed adducts. The optical density of the solutions was measured using a light filter with λ_{max} = 480 nm. The presence of two inflection points on the saturation curve allows us to propose a stepwise formation of the adducts **1**:**3** (1:1 and 2:1). The predominant formation of 2:1 adducts in the conditions of excess compound **1** is indicated by the dependence of the curve for the optical density versus the ratio of reagents for isomolar series of substances.

The IR spectra recorded for a solution of the uncolored compound from anhydride **2** and imidazole **1**, prepared from the solution in acetonitrile, contains two intense absorption bands at 1740 cm^{-1} (solution in methanol) or 1735 cm^{-1} (KBr dispersion) which can be assigned to a stretching vibration of the carboxylic groups and also bands at 1620 (methanol) and 1610 cm^{-1} (KBr), the shoulder in 1650 cm^{-1} region assigned to an amide group. The protonation constant of the precipitated compound ($pK_a = 3.3$) was determined by potentiometric titration [5]. It is known that, for imidazole **1** $pK_a = 7.69$ [6] and for maleic and fumaric acids 1.92 and 3.02 respectively [7]. The compound separated based on the anhydride **2** has $pK_a = 2.73$ which is close to the known value for phthalic acid $pK_{aI} = 2.58$ [7]. The colored compound based on anhydride **3** was prepared and separated from concentrated solutions of the reagents (mp > 170°C, $\lambda_{max} = 480$ nm). The material is a dark colored powder, readily soluble in water and poorly dispersed in KBr.

One should again stress the difference in the reaction course for imidazole **1** with anhydrides **2** and **3**. In the first case the reaction rate is comparatively high and there are formed a colored product soluble in acetonitrile and then a white precipitate, whereas in the second a change in color of the solution is not observed. At the same time, the final products in both cases are compounds with identical functional carboxyl and amide groups.

A study of the reaction of maleic anhydride with primary and secondary amines has shown [8] that the formation of a zwitterionic form is the stage which determines the rate of the reaction.

In the general case, the reaction of reagents **1** and **3** in solution gives π-molecular complexes of several types (**1,3; 4,3; 6-1, 6-4**). This description for the formation of the π-complex **7** agrees with the data in the study [9]. In addition, there is observed a series of electronic absorption bands for the reaction solutions which can be related to a scheme for consecutive formation of molecular complexes. The existence of the molecular complex **7** is the reason for the differences in the course of the reaction. In fact, its formation depends on the relation between the energy of the lowest unoccupied orbital of the acceptor and the highest occupied molecular orbital of the donor molecule. According to [10] the values of the polarographic wave potentials in DMF are $E_{1/2} = 0.88$ in **3** and $E_{1/2} = 1.36$ in **2**. It follows that anhydride **3** must form a quite stable molecular complex with imidazole **1** whereas it is practically not formed with anhydride **2**.



On this basis were propose that, depending on reaction conditions, the anhydride **3** and imidazole **1** can form an acid amide or a molecular complex. In the first case the limiting stage is evidently the formation of the zwitterion **8** and in the second it is the molecular complex **7**.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 983G instrument using KBr cuvettes with a thickness of 0.1 mm and electronic absorption spectra on a Specord UV-vis instrument in 1 cm quartz cuvettes. Optical densities of solutions were measured on a Spectromom 210 instrument in 1 cm cuvettes. Potentiometric titrations were carried out on a Mettler DL-40RC autotitrator with glass and calomel electrodes.

In this work we used phthalic anhydride with a basic material content of 99.8% and maleic anhydride with a content of 99.2%; the anhydride purity was calculated *via* reaction with piperidine [11]. Acetonitrile and dimethylformamide (both chemical pure grade) were used as solvents. Technical 2-methylimidazole was recrystallized from ethanol.

The white precipitate formed in acetonitrile upon reaction of anhydride **3** with imidazole **1** at a reagent concentration of 0.5-1.5% was filtered off and dried in vacuo at 60°C over 1 h. The compound from anhydride **2** and imidazole **1** was obtained similarly but at higher concentration (>5%). The colored compound from anhydride **3** and imidazole **1** was prepared by heating in DMF at a concentration of reagents above 5%. After decanting the solvent, the precipitate which was obtained as a gelatinous mass was dried in vacuo at 60°C for 2 h.

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