High-Pressure Fourier Transform Infrared Spectroscopy Study of the Diels–Alder Reaction of Isoprene and Maleic Anhydride in Supercritical Carbon Dioxide

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Synopsis. A high-pressure FTIR spectroscopy was used to make an in situ study on the Diels–Alder reaction of isoprene and maleic anhydride catalyzed with aluminum chloride in supercritical carbon dioxide at 306 K and 7.45 and 7.85 MPa, suggesting a two-step mechanism and showing a pressure effect.

Considerable attension has recently been focused on the highly compressible properties of supercritical fluids (SCFs) in the near-critical region from scientific and industrial points of view.[1–5] The solvent strength varies widely with both the pressure and temperature in that region; this sensitivity can be applied to the control of chemical reaction processes. A few studies have shown that the use of SCFs as reaction media leads to significant increases in the reaction rates and the variation in product distributions.[1,2,6–8] However, detailed studies have rarely been made to examine the elementary processes involved in reactions in SCFs.[9] This is mainly because it is difficult to follow reactions in situ under supercritical conditions.

In the present work, high-pressure Fourier transform infrared (FTIR) spectroscopy was applied to a study of a chemical reaction in supercritical carbon dioxide. The reaction that we conducted was a Diels–Alder reaction of isoprene and maleic anhydride catalyzed with aluminum chloride. It was followed by examining changes in the absorption intensities for some functional groups characteristics to both the reactants and product. The present note presents information concerning the mechanism of the reaction under supercritical conditions and demonstrates that the FTIR technique used in this work is promising for the study of chemical reactions in SCFs.

Details of the experimental system used, including a high-pressure cell that can withstand high pressures and temperatures such as 50 MPa and 373 K, was described elsewhere.[10] A 2.94 g (0.03 mol) of maleic anhydride with 0.40 g (0.003 mol) of aluminum chloride was dissolved in 20 ml of benzene. A 0.35 μL portion of this solution and 0.15 μL of isoprene were simultaneously injected into the system from two injection valves. The reactants reached the high-pressure flow cell immediately after injection by stopping the flow. The reaction was conducted at 306±0.1 K and at 7.45 and 7.85 MPa. During the reaction, FTIR measurements were made at certain time intervals. Interferrograms were accumulated at a rate of 1 scan per 1.2 s and 4—5 scans were made for each measurement. A spectrum of supercritical carbon dioxide alone was used to provide the background spectrum.

Figure 1 shows the changes in the intensities of the absorption bands at 1597, 1784, and 1798 cm^{-1} during the reaction. The bands at 1597 and 1784 cm^{-1} can be

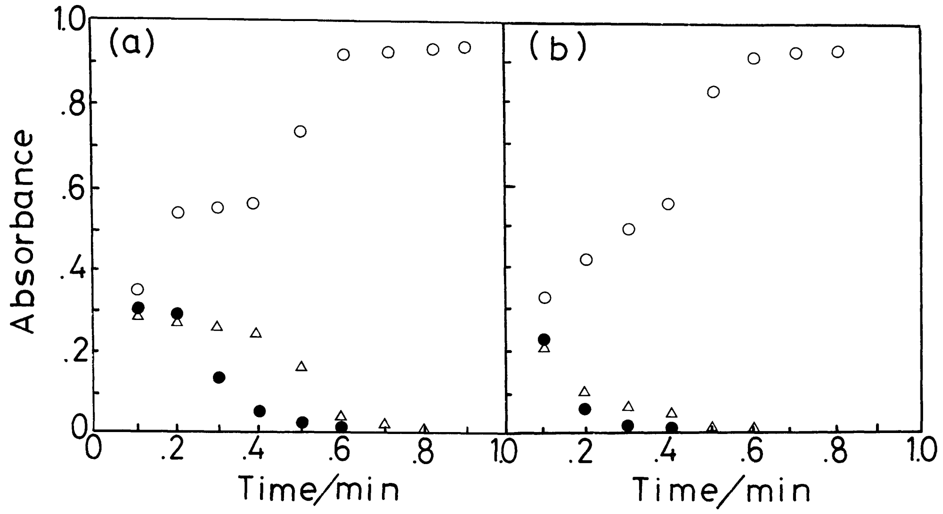
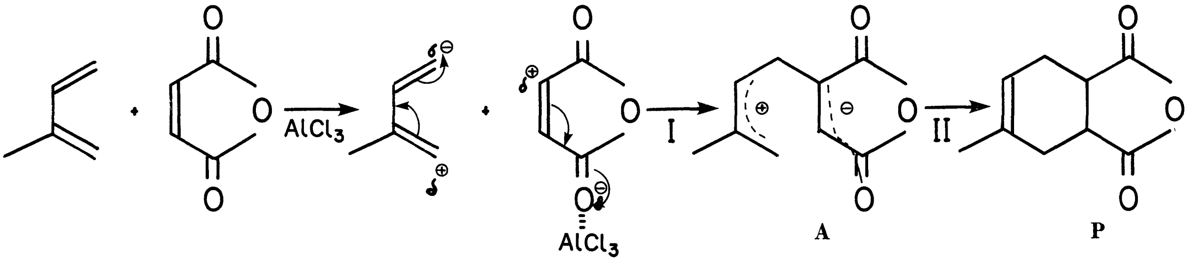


Fig. 1. Changes of the intensities of the absorption bands at 1597 (●), 1798 (○), and 1784 cm^{-1} (△) with time on the Diels–Alder reaction of maleic anhydride and isoprene catalyzed with aluminum chloride in supercritical carbon dioxide at 306 K. Pressure: (a) 7.45 MPa; (b) 7.85 MPa.



Scheme 1.

assigned to a C=C stretching of the isoprene and a C=O stretching of the maleic anhydride, respectively. From a NMR measurement, compound (**P**) shown in Scheme 1 was proved to be the only product in the present cycloaddition. The absorption at 1798 cm^{-1} is assigned to C=O stretching of this product. The formation of a cyclic adduct increases the frequency of the C=O stretching absorption band as a result of conjugation. Figure 1(a) indicates that the absorbance at 1597 cm^{-1} decreased and disappeared at about 0.6 min and that at 1784 cm^{-1} gradually decreased during a period of 0.2—0.4 min and then decreased more rapidly, disappering after about 0.6 min. The absorbance at 1798 cm^{-1} increased until 0.2 min, remained almost unchanged during the period from 0.2—0.4 min, and then increased again, reaching a constant value. The results at a higher pressure of 7.85 MPa are given in Fig. 1(b), showing some pressure effect; the absorbance at 1597 and 1784 cm^{-1} disappeared within a shorter time, and that at 1798 cm^{-1} increased throughout the reaction until about 0.5 min and attained the same constant value within a shorter time as compared with the reaction at 7.45 MPa. It follows that the overall reaction rate was enhanced by increasing the pressure from 7.45 to 7.85 MPa.

It is commonly said that Diels-Alder reactions proceed via a one-step, concerted mechanism under ordinary conditions.[11] However, the results shown in Fig. 1 strongly suggest a two-step mechanism for the present Diels–Alder reaction in carbon dioxide under supercritical conditions. The step-wise increase in the intensity of the 1798 cm^{-1} absorption during the reaction would be indirect evidence for the presence of some intermediate. One possible explanation for the changes in the absorbance shown in Fig. 1 is that the reaction proceeds via the two steps shown in Scheme 1: the formation of one σ-bond giving an intermediate (**A**), followed by a ring closure, yielding the cycloadduct (**P**). The observed step-wise increase of the 1798 cm^{-1} absorption is believed to correspond to the formation of two σ-bonds in the two steps. A gradual decrease in the C=O absorbance at 1784 cm^{-1} of maleic anhydride, as observed more clearly at 7.45 MPa, also suggests that the intermediate has two C=O bonds, similar to those of maleic anhydride and the product. One might expect that the IR carbonyl stretching frequency and band intensity for (**A**) are different from those for (**P**). The present FTIR measurements, however, did not support this idea.

In a few cases of Lewis-acid catalyzed cycloadditions, the mechanism of a [2+2] addition followed by a rearrangement, giving a [2+4] adduct, was reported in the literature.[12] Such a mechanism might be possible for the present Diels–Alder reaction. However, the intermediate that can be expected from this mechanism could not well support the FTIR results of Fig. 1. Also, the present reaction takes place with thermal energy; it is therefore natural to believe that it proceeds through a [2+4] addition mechanism. We presently believe that Scheme 1 is a possible tentative mechanism for the Diels–Alder reaction in supercritical carbon dioxide; further work is required to obtain a definite conclusion. Since the reaction is carried out under unordinary conditions, we should consider the solvent properties of carbon dioxide at supercritical conditions.

Regarding the influence of increasing pressure, the results in Fig. 1 show an enhancement in the overall reaction rate. If one can adopt the mechanism shown in Scheme 1, it is speculated that the second step depends more strongly on the pressure than does the first step, since the change of the 1798 cm^{-1} absorbance during the initial stage of the reaction seems to be little influenced by the pressure. It is a current subject of study to examine the effects of the pressure of SCFs on the reactions and to clarify the key physical/chemical properties governing the effects.

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