termediate in the $Fe(CO)_5$-catalyzed WGSR proceeds via dianion **2** and requires base catalysis.

Note Added in Proof. While this manuscript was in press, two important developments have occurred. We recently found the hydroxide–*ammonia* cluster ion, $OH(NH_3)^-$, reacts with $Fe(CO)_5$ to yield, inter alia, $(CO)_4FeH^-$ as a primary product. Evidently, NH_3-catalyzed decarboxylation may occur within an ion–molecule complex such as that depicted in eq 12, provided excess internal energy from the initial OH^- attachment is available. Furthermore, a recent reinvestigation of $Fe(CO)_5$ in *nonaqueous* OH^- solutions has come to our attention which points to a protic solvent-catalyzed mechanism for $Fe(CO)_4COOH^-$ decarboxylation. We thank Professor P. C. Ford for stimulating discussion and a preprint of these results.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Research Corporation for the support of this research. We are especially grateful to T. Ridley for transforming our instrument blueprints into reality.

Registry No. 1, 90367-71-8; $Fe(CO)_5$, 13463-40-6; OH^-, 14280-30-9; $OH^-\cdot H_2O$, 23138-14-9; $OH^-\cdot 2H_2O$, 34118-36-0; $OH^-\cdot 3H_2O$, 34118-37-1; $OH\cdot 4H_2O$, 24823-52-7.

Stereoselective Exchange Kinetics of L- and D-Histidines for Cl^- in the Interlayer of a Hydrotalcite-like Compound by the Chemical Relaxation Method

Tetsuya Ikeda, Hironori Amoh, and Tatsuya Yasunaga*

Contribution from the Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan. *Received January 30, 1984*

Abstract: The ion-exchange kinetics of L- and D-histidines for Cl^- in aqueous suspensions of Mg–hydrotalcite-like compound were studied by using the pressure-jump relaxation method with electric conductivity detection. Two relaxation phenomena were observed in both systems, and it was found that the difference in the L- and D-histidines as optical isomers appeared in both kinetic and static data. The fast relaxation was attributed to the release process of Cl^- in the interlayer induced by the histidine adsorption, while the slow relaxation was attributed to an intercalation process of histidine into the interlayer of the Mg–hydrotalcite-like compound. Kinetic and static parameters were determined and revealed differences between the ion-exchange properties of the L and D forms. The rate constants obtained for the D-histidine system were smaller than those for L-histidine, indicating a preference for that form. This result will give us a clue to understanding the origin of the chirality of living systems.

The stereoselective adsorption–desorption of molecules on clays may be related to the origin of chirality in living systems.[1-3] Several investigations have recently reported that clays preferentially adsorb one of the optical isomers. By studying the stereoselectivity of clays in the adsorption of optical isomers, we hoped that the role of clay minerals in chemical evolution might be clarified. However, the mechanism of adsorption–desorption of optical isomers has not been successfully determined because of the difficulties in studying these systems.

One of the interesting properties of layered compounds such as zeolite, montmorillonite, and hydrotalcite is their ability to selectively intercalate molecules into the interlayer regions.[4] This is particularly true for montmorillonite and hydrotalcite, which have shape-selective catalytic properties that can be changed by varying the interlayer distance. In previous papers,[5-10] ion-exchange and intercalation kinetics have been studied in zeolite, montmorillonite, and hydrotalcite aqueous systems. The results of these studies have confirmed the shape-selective properties of these clays for exchanging molecules.

In the present study, kinetic evidence is presented showing the preference of a Mg–hydrotalcite-like compound for a L-histidine isomer over a D-histidine isomer, in aqueous solutions. It is hoped that this study will provide important information with respect to the use of clays as catalysts for producing one of the optical isomers and the origin of asymmetry in biological systems.

Experimental Section

Kinetic measurements were carried out by using the pressure-jump apparatus with an electric conductivity detecting system. The details of the measurements of relaxation signals using the present apparatus and conductivity detection have been described elsewhere.[11] The time constant of the pressure jump is 80 μs.

The Mg–hydrotalcite-like compound ($Mg_{0.7}Al_{0.3}(OH)_2(CO_3)_{0.15}nH_2O$) was supplied from the Kyowa Chemical Co.[12] The chloride type of the Mg–hydrotalcite-like compound, Mg–HT(Cl), used was prepared by ion exchange of Cl^- for CO_3^{2-} in Mg–HT(CO_3) and was washed several times with distilled water. The anion-exchange capacity was determined to be 100 mequiv/100 g from the OH^- titration. The Mg–HT(Cl) particles were dispersed in aqueous solution by ultrasonication and formed very stable suspensions under the present experimental condition. Microscopic examination confirmed that the mean diameter of the Mg–HT(Cl) particles is less than 1 μm.

The amounts of L- and D-histidines adsorbed were determined indirectly from the concentration change in the supernatant solution by means of the colorimetric ninhydrin method at a wavelength of 570 nm. Before the measurements, samples of the Mg–HT(Cl) suspensions containing L- and D-histidines were centrifuged for 40 min at 20000g in order to settle the particles completely. The concentrations of H^+ and Cl^- were determined with a glass electrode and a Cl electrode, respectively.

(1) Kachalski, A. *Nature (London)* **1970**, *228*, 636.
(2) Degens, E. T.; Matheja, J.; Jackson, T. A. *Nature (London)* **1970**, *227*, 492.
(3) Yamagishi, A. *J. Phys. Chem.* **1982**, *86*, 2472.
(4) "Intercalation Chemistry"; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982.
(5) Ikeda, T.; Sasaki, M.; Yasunaga, T. *J. Phys. Chem.* **1983**, *87*, 745.
(6) Ikeda, T.; Sasaki, M.; Yasunaga, T. *J. Phys. Chem.* **1982**, *86*, 1680.
(7) Ikeda, T.; Nakahara, J.; Sasaki, M.; Yasunaga, T. *J. Colloid Interface Sci.* **1984**, *97*, 278.
(8) Ikeda, T.; Sasaki, M.; Yasunaga, T. *J. Colloid Interface Sci.* **1984**, *98*, 192.
(9) Ikeda, T.; Yasunaga, T. *J. Colloid Interface Sci.* **1984**, *99*, 183.
(10) Ikeda, T.; Yasunaga, T. *J. Phys. Chem.* **1984**, *88*, 1253.
(11) Hachiya, K.; Ashida, M.; Sasaki, M.; Kan, H.; Inoue, T.; Yasunaga, T. *J. Phys. Chem.* **1979**, *83*, 1866.
(12) Miyata, S. *Clays Clay Miner.* **1975**, *23*, 369.

0002-7863/84/1506-5772$01.50/0

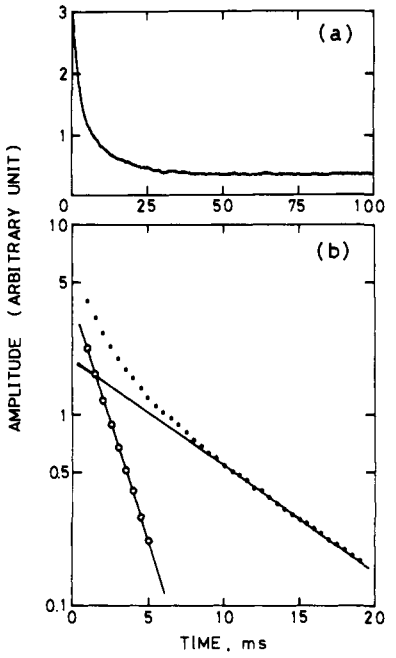

Figure 1. (a) Typical relaxation curve observed in the Mg–HT(Cl)–L- and D-histidine systems by using the pressure-jump relaxation method with electric conductivity detection at the particle concentration of 15 g dm^{-3} and 25 °C. (b) Semilogarithmic plot of the relaxation curve.

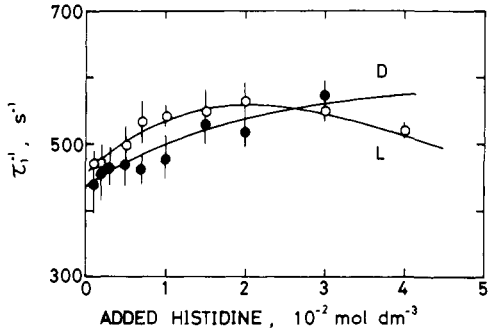

Figure 2. Dependences of the fast reciprocal relaxation time on the added L-histidine (○) and D-histidine (●) concentrations in aqueous suspensions of Mg–HT(Cl) at the particle concentration of 15 g dm^{-3} and 25 °C.

The particle concentration of all samples was 15 g dm^{-3}, and the samples were equilibrated for 24 h after preparation. All preparation and experimentation was done in a nitrogen atmosphere, and the temperature was controlled at 25 °C.

Results and Discussion

Figure 1a shows a typical relaxation curve observed in aqueous suspensions of the Mg–HT(Cl)–L- and D-histidine systems in the pH range 8.5–9.1 by using the pressure-jump relaxation method with electric conductivity detection. The direction of the relaxation signal indicates a decrease in the conductivity of the suspension during the relaxation. No relaxation was observed in a Mg–HT(Cl) suspension of the same pH or in the supernatant solution of the Mg–HT(Cl)–L- and D-histidine systems. The semilogarithmic plot of a typical relaxation curve in Figure 1b shows that the relaxation curve consists of two relaxation processes. The dependences of the fast and slow relaxation times (τ_1^{-1} and τ_2^{-1}) on the concentrations of added L- and D-histidines in aqueous suspensions of the Mg–HT(Cl) are shown in Figures 2 and 3, respectively. As can be seen from these figures, the values of τ_1^{-1} increase with increasing concentration of added histidine and decrease in the high-concentration range, while the values of τ_2^{-1} in both systems increase with increasing concentration of added histidine and approach constant values. When the two relaxations observed are accounted for, the ion exchange of histidine for Cl^- in Mg–HT(Cl) may consist of at least two elementary processes. In order to determine the mechanism, the equilibrium properties

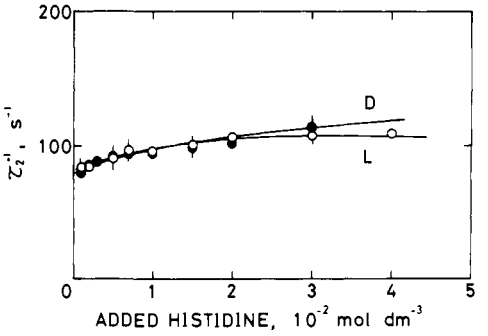

Figure 3. Dependences of the slow reciprocal relaxation time on the added L-histidine (○) and D-histidine (●) concentrations in aqueous suspensions of Mg–HT(Cl) at the particle concentration of 15 g dm^{-3} and 25 °C.

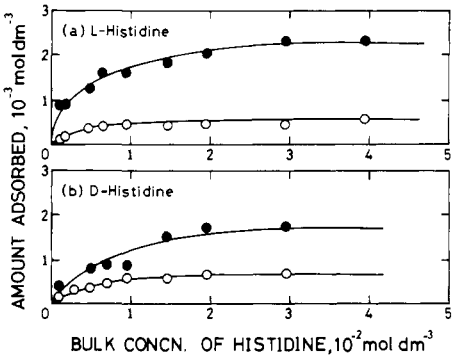

Figure 4. Adsorption isotherms of histidines (○) and the amounts of Cl^- released (●) in the (a) Mg–HT(Cl)–L-histidine system and the (b) Mg–HT(Cl)–D-histidine system at the particle concentration of 15 g dm^{-3} and 25 °C. The bulk concentration of histidine determined by means of a colorimetric analysis is the sum of [His^-] and [His^{+-}].

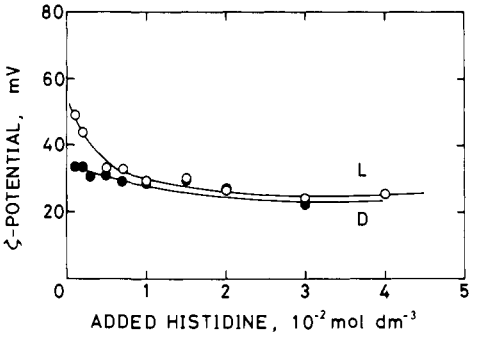

Figure 5. Electrophoretic measurements of the ζ potential of the Mg–HT(Cl) particles as a function of the concentrations of L-histidine (○) and D-histidine (●).

of the Mg–HT(Cl)–L- and D-histidine systems were also investigated.

Figure 4 shows the adsorption isotherms of L- and D-histidines onto the Mg–HT(Cl) particles in aqueous suspensions, where the bulk concentration of histidine is mainly the sum of the anion and zwitterion forms of histidine in the present pH range of 8.5–9.1. In the present systems, ion exchange of histidine for Cl^- occurred as was apparent from Cl^--release data. The amount of Cl^- released was determined by using a Cl electrode and is also shown in Figure 4. These results confirm that L- and D-histidine adsorption is intercalated into the interlayer regions of Mg–HT(Cl). When the amount of histidine adsorbed is compared with the amount of Cl^- released in Figure 4, it can be seen that the amount of histidine adsorbed is less than that of Cl^- released. The dependences of the ζ potential on the concentration of L- and D-histidines are shown in Figure 5, in which the positive value of the ζ potential in aqueous suspensions of Mg–HT(Cl) is due to the positively charged vacant site of Cl^- released. As can be seen from this figure, the fact that these values keep nearly a constant value

Table I. Values of the Rate and Equilibrium Constants of Ion Exchange of L- and D-Histidines for Cl^- in Aqueous Suspensions of Mg–HT(Cl) at 25 °C

form	k_1^{int}, mol^{-1} dm^3 s^{-1}	k_{-1}^{int}, s^{-1}	k_2^{int}, s^{-1}	k_{-2}^{int}, mol^{-1} dm^3 s^{-1}	K_1^{int}, mol^{-1} dm^3	K_2^{int}, mol dm^{-3}	K_{Cl}^{int}
L	$(1.4 \pm 0.1) \times 10^2$	$(5.4 \pm 0.1) \times 10$[a]	$(5.0 \pm 0.3) \times 10^2$	$(2.7 \pm 0.2) \times 10^4$	2.6 ± 0.2[b]	$(1.9 \pm 0.3) \times 10^{-2}$	$(5.0 \pm 0.5) \times 10^{-2}$
D	$(9.8 \pm 0.3) \times 10$	$(2.5 \pm 0.3) \times 10$[a]	$(5.0 \pm 0.3) \times 10^2$	$(2.7 \pm 0.2) \times 10^4$	3.9 ± 0.4[b]	$(1.9 \pm 0.3) \times 10^{-2}$	$(7.5 \pm 0.3) \times 10^{-2}$

[a] See eq 2. [b] See eq 8.

indicates that the adsorption–desorption of L- and D-histidines onto the vacant site is negligible. Since an ion-exchange reaction of OH^- for Cl^- in basic aqueous suspensions of the Mg–HT(Cl) can also take place,[13] it is suggested that the Cl^- release exceeding the amount of histidine adsorption may be also caused by the following reaction through the hydrolysis of added histidine:

$$S(Cl) + OH^- \rightleftharpoons S(OH) + Cl^- \quad (I)$$

$$His^- + H_2O \overset{K_B}{\rightleftharpoons} His^{+-} + OH^- \quad (II)$$

with

$$K_B = \frac{[His^{+-}][OH^-]}{[His^-]} \quad (1)$$

where S(Cl) and S(OH) denote the adsorbed states of Cl^- and OH^- in the interlayer of Mg–HT(Cl). K_B is the equilibrium constant of the hydrolysis of histidine in the bulk phase. Thus, the two kinds of the anion-exchange sites relate to the present ion-exchange reaction.

Next, consider the following mechanism of ion-exchange with L- and D-histidines at the particle surface in aqueous suspensions of Mg–HT(Cl):

$$S(Cl) \underset{k_{-1}}{\overset{K_1}{\underset{k_1}{\rightleftharpoons}}} S(Cl\cdot His) \underset{k_{-2}}{\overset{K_2}{\underset{k_2}{\rightleftharpoons}}} S(His) \quad (III)$$

His^- (step 1) Cl^- (step 2)

$$S(OH) + His^- \underset{k_{-3}}{\overset{K_3}{\underset{k_3}{\rightleftharpoons}}} S(His) + OH^- \quad (IV)$$

step 3

with

$$K_1 = k_1/k_{-1} = [S(Cl\cdot His)]/([S(Cl)] \times [His^-]_s) \exp(e\Psi_\beta/k_BT) = K_1^{int} \exp(e\Psi_\beta/k_BT) \quad (2)$$

$$K_2 = k_2/k_{-2} = [S(His)] \times [Cl^-]_s/[S(Cl\cdot His)] \exp(-e\Psi_\beta/k_BT) = K_2^{int} \exp(-e\Psi_\beta/k_BT) \quad (3)$$

$$K_3 = k_3/k_{-3} = [S(His)][OH^-]_s/([S(OH)][His^-]_s) \quad (4)$$

where the symbols S(Cl·His) and S(His) denote the adsorbed state of both Cl^- and His^- on the Mg–HT(Cl) surface and the released state of Cl^- induced by the His^- intercalation. $k_{\pm i}$ and K_i (i = 1, 2, 3) are the rate and equilibrium constants, respectively. Ψ_β is the surface potential created by the adsorptions of of His^- and Cl^-.[14] The subscript s and the superscript int stand for the surface and intrinsic, respectively, k_B is the Boltzmann constant, and T is the absolute temperature.

For the above reactions, the values of the equilibrium constants can be obtained from the following relationship:

$$\frac{[S(His)][OH^-]}{[S(OH)][His^-]} = K_{Cl}^{int}\frac{[S(Cl)][OH^-]}{[S(OH)][Cl^-]} + K_3^{int} \quad (5)$$

with

$$K_{Cl}^{int} = K_1^{int}K_2^{int} \quad (6)$$

(13) Sasaki, M.; Mikami, N.; Ikeda, T.; Hachiya, K.; Yasunaga, T. *J. Phys. Chem.* **1982**, *86*, 4413.

(14) Davis, J. A.; James, R. O.; Leckie, J. O. *J. Colloid Interface Sci.* **1978**, *63*, 480.

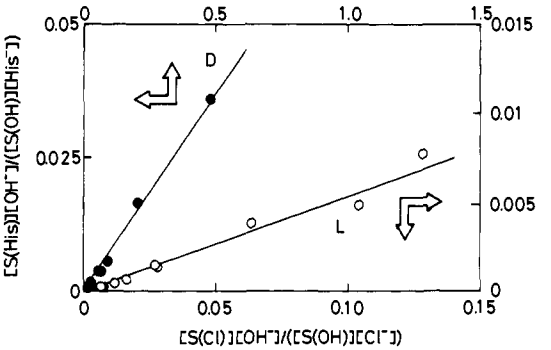

Figure 6. Plots of $[S(His)][OH^-]/([S(OH)][His^-])$ vs. $[S(Cl)][OH^-]/([S(OH)][Cl^-])$ in eq 5.

The plot of eq 5 shown in Figure 6 yields a straight line through the origin in each system, indicating that the mechanism proposed is statistically plausible. Furthermore, it is clear from this figure that reaction IV is negligible under the present experimental condition and that the amount of the intermediate state in reaction III is less than that of S(Cl) and S(His). The value of the equilibrium constant of the overall reaction III is listed in Table I.

Under the assumption that reaction II is much faster than steps 1 and 2 and that step 2 is faster than step 1, the fast and slow relaxation times in which the surface potential is taken into account are given by

$$\tau_1^{-1} = k_2^{int} \exp\left(-\frac{e\Psi_\beta}{2k_BT}\right) + k_{-2}^{int} \exp\left(\frac{e\Psi_\beta}{2k_BT}\right)([S(His)] + [Cl^-]) \quad (7)$$

$$\tau_2^{-1} = k_1^{int} \exp\left(\frac{e\Psi_\beta}{2k_BT}\right) \times \left([His^-] + [S(Cl)]\frac{[His^{+-}] + [OH^-]}{K_B + [His^{+-}] + [OH^-]}\right) + k_{-1}^{int} \exp\left(-\frac{e\Psi_\beta}{2k_BT}\right)\frac{[S(His)] + [Cl^-]}{K_B + [S(His)] + [Cl^-]} = k_1^{int} \exp\left(\frac{e\Psi_\beta}{2k_BT}\right)\left([His^-] + [S(Cl)]\frac{[His^{+-}] + [OH^-]}{K_B + [His^{+-}] + [OH^-]} + \frac{[S(His)] + [Cl^-]}{K_1(K_2 + [S(His)] + [Cl^-])}\right) \quad (8)$$

The plot of eq 7 shown in Figure 7 yields a straight line for both systems of L- and D-histidines, justifying that the fast relaxation observed may be attributed to step 2. The values of the rate constants k_2^{int} and k_{-2}^{int} were obtained from the intercept and the slope of the obtained straight line and are listed in Table I. The value of the equilibrium constant K_2^{int} was calculated from the ratio of the obtained rate constants and is also listed in Table I. On the other hand, the plots for the slow relaxation time in the same procedure yield straight lines, having small values of k_1^{int} compared to the other concentration terms. Therefore, one must plot τ_2^{-1} vs. the concentration term in eq 8 in which the value of K_1 is estimated from the previously obtained values of K_{Cl}^{int} and K_2^{int}. As can be seen from Figure 8, the plots of eq 8 yield straight

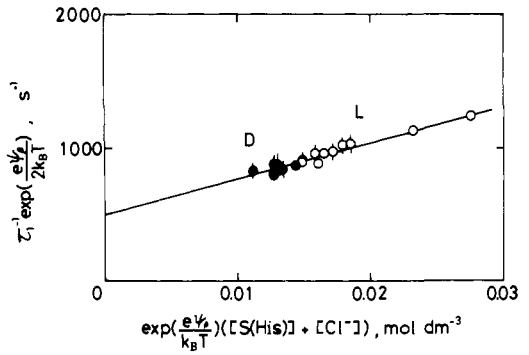

Figure 7. Plots of $\tau_1^{-1} \exp(e\Psi_\beta/2k_BT)$ vs. $\exp(e\Psi_\beta/k_BT)([S(His)] + [Cl^-])$ in eq 7.

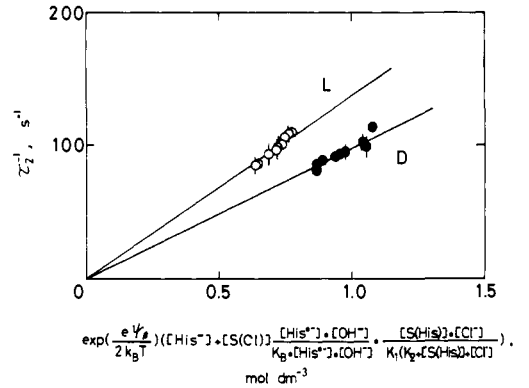

Figure 8. Plots of τ_2^{-1} vs. the concentration term in eq 8.

lines through the origin in both the Mg–HT(Cl)–L- and D-histidine systems. The value of the rate constant k_1^{int} was obtained from the slope of the straight line, and the value of the rate constant k_{-1}^{int} was evaluated by using the equilibrium constant K_1^{int}. The values of the rate constants obtained are also given in Table I. The good linearities for both the L- and D-histidine systems shown in Figures 7 and 8 lead to the conclusion that the two relaxations observed can be reasonably attributed to reaction III.

From the comparison of the obtained rate constants, one can see that the difference in the rate constants of the optical isomers is revealed in the value of the intercalation–deintercalation rate of step 1. It appears that the intercalation–deintercalation rate of L- and D-histidines is governed mainly by the geometric factors of the interlayer spacing and the intercalating molecule, since the size of the interlayer spacing of Mg–HT(Cl) is nearly equal to that of intercalating histidine. In the present study, Table I shows that the value of the rate constants of the intercalation–deintercalation of D-histidine is less than that for L-histidine. Taking into account that the values of the rate constants of step 2 for L-histidine are the same as that for D-histidine, it is concluded that the difference in the kinetic and static data may be due to the difference in the rates of the intercalation–deintercalation of L- and L-histidines, resulting from the different chirality of the optical isomers.

Finally, it can be seen from the present study that the stereoselective adsorption of the configurational isomers of L- and D-histidines was achieved by the Mg–hydrotalcite-like compound despite the fact that the clay itself is optically inactive. This fact indicates that the stereoselectivity of the hydrotalcite clay must be due to properties in the interlayer region. The results of this study show that the selectivity of clays for biological significant isomers results from differences in rates of intercalation. The reasons for the selection of L-amino acid by the Mg–hydrotalcite-like compound and, in general, the selection of the L form in biological systems may be revealed by further studies in which the properties of the interlayer region are varied.

Registry No. Cl^-, 16887-00-6; L-histidine, 71-00-1; D-histidine, 351-50-8.

[2 + 1] Cycloaddition of Ketene Radical Cation and Ethylene

Chhabil Dass and Michael L. Gross*

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588. *Received January 9, 1984*

Abstract: The reaction of the ketene radical cation and neutral ethylene has been investigated by using tandem mass spectrometry and Fourier transform mass spectrometry. The reaction was conducted at high pressures (150–500 mtorr) in the presence of an inert bath gas which permitted collisional stabilization and isolation of the adduct for study by collisionally activated dissociation (CAD) and metastable ion spectroscopy. The structure of the adduct was established to be that of the cyclobutanone radical cation. Thus, the mechanism of the reaction is a facile [2 + 1] cycloaddition across the carbon–carbon double bond of the ketene radical cation.

Studies of cycloadditions of neutral molecules have substantially increased our understanding of pericyclic reactions. Their mechanisms have been impressively accounted for by the Woodward–Hoffman rule[1] and by the frontier molecular orbital (FMO) approach developed by Fukui.[2] However, few reports have appeared in the literature that describe cycloaddition reactions involving radical cations as one of the reactants. In 1969, Ledwith et al.[3] were first to demonstrate a radical cation catalyzed cyclodimerization. Recently, Bauld and co-workers[4,5] have shown convincingly that ionization of one partner has considerable advantage in enhancing the rate of cycloaddition. Similar observations have been made by us[6] and others.[7]

However, the mechanistic aspects of cycloaddition reactions involving radical cations are not yet perfectly understood. The

(1) Woodward, R. B.; Hoffmann R. *J. Am. Chem. Soc.* **1965**, *87*, 395.
(2) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.
(3) Bell, F. A.; Crellin, R. A.; Fujii, N.; Ledwith, A. *Chem. Commun.* **1969**, 251.
(4) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. Bauld, N. L.; Pabon, R. *Ibid.* **1983**, *105*, 634.
(5) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. Bauld, N. L.; Bellville, D. J. *Ibid.* **1982**, *104*, 2665.
(6) Dass, C.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5724. Gross, M. L.; Russell, D. H. *Ibid* **1979**, *101*, 2082.
(7) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577.

0002-7863/84/1506-5775$01.50/0