for catalyst A. To the incubated catalyst was added 0.153 g of a (1.21 ± 0.02):1 mixture of decadiene-d_0 and -d_6 (determined by weight and mass spectral analysis). At four time intervals, 10-mL gas samples were withdrawn and replaced with an equal volume of argon. The gas was injected into the preparative gas column mentioned above and *cis*-2-butenes were isolated with a glass trap cooled in liquid N_2 at the exit port. The trapped butenes were then submitted for mass spectral analysis. The d_3-/d_6-C_4 ratios listed in Table VI were found by comparing the peak heights at *m/e* 59 (d_3-C_4) and 62 (d_6-C_4). Liquid aliquots were withdrawn and the 2,8-decadiene was isolated by preparative GLC with the DC-550 column mentioned above. These samples were analyzed via mass spectroscopy, and the peak heights at *m/e* 138 (d_0-C_{10}), 141 (d_3-C_{10}), and 144 (d_6-C_{10}) were compared. No other peaks in this region were noted. The d_3-/d_6-C_{10} ratios were found and are recorded in Table VI. The *t*-/*c*-C_4 ratio was determined at each gas and liquid sampling and are also listed in Table VI.

Metathesis of a (2.68 ± 0.05):1 Mixture of *cis,cis*-2,8-Decadiene-d_0:-d_6. In the same way as described above, 0.120 g of a (2.68 ± 0.05):1 mixture of *cis,cis*-2,8-decadiene-d_0:-d_6 was added to catalyst A. After 10 min two 20-mL gas samples were withdrawn from the tube and the reaction was immediately quenched with 0.5 mL of H_2O. The 2-butenes were isolated in the same way and the collection tube was submitted for analysis. A d_0:d_3:d_6 ratio of 1:(0.72 ± 0.06):(0.18 ± 0.03) was found. The calculated carbene ratio is 1:(0.75 ± 0.04):(0.14 ± 0.02), and the ratio for the pairwise scheme is 1:(0.64 ± 0.02):(0.17 ± 0.02). The *t*-/*c*-C_4 ratio was 0.31 ± 0.04, which corresponds to about 6-8% conversion of starting material. Using *n*-decane as an internal liquid standard, the yield of cyclohexene was found to be 5 ± 2% based on decadiene.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. This manuscript is taken in part from the thesis of C. R. Hoppin.

References and Notes

(1) (a) N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem., Int. Ed. Engl.*, **15**, 401 (1976); (b) J. C. Mol and J. A. Moulin, *Adv. Catal.*, **24**, 131 (1975); (c) R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, **4**, 155 (1975), (d) R. H. Grubbs in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., American Elsevier, New York, 1976, p 423; (e) T. J. Katz, *Adv. Organomet. Chem.*, **16**, 283 (1977).

(2) (a) R. H. Grubbs, D. D. Carr, and P. L. Burk, *J. Am. Chem. Soc.*, **97**, 3265 (1975); (b) R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *ibid.*, **98**, 3478 (1976).

(3) (a) T. J. Katz and R. Rothchild, *J. Am. Chem. Soc.*, **97**, 2519 (1975); (b) T. J. Katz and J. McGinnis, *ibid.*, **99**, 1903 (1977); (c) J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970).

(4) J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Am. Chem. Soc.*, **98**, 605 (1976).

(5) J. L. Bilhou, J. M. Basset, R. Mutin, and W. F. Graydon, *J. Am. Chem. Soc.*, **99**, 4083 (1977).

(6) W. B. Hughes, *Chem. Commun.*, 431 (1969).

(7) J. M. Basset, *J. Am. Chem. Soc.*, **97**, 7376 (1975).

(8) (a) E. A. Zeuch, *Chem. Commun.*, 1182 (1968); (b) P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *J. Chem. Soc., Chem. Commun.*, 1221 (1972).

(9) M. T. Mocella, R. Rovner, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 4689 (1976).

(10) Much of the 2-butene formed during these reactions remains dissolved in the solvent and appropriate GLC calibrations were employed for the analysis of the gaseous 2-butene.

(11) R. H. Grubbs and C. R. Hoppin, *J. Chem. Soc., Chem. Commun.*, 634 (1977).

(12) T. J. Katz and W. H. Hersh, *Tetrahedron Lett.*, 585 (1977).

(13) M. LeConte, J. L. Bilhou, W. Reimann, and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 341 (1978).

(14) (a) J. M. Basset, G. Coudurier, R. Mutin, and H. Praliaud, *J. Catal.*, **34**, 152 (1974); (b) G. Doyle, *ibid.*, **30**, 118 (1973).

(15) At conversions of 10% the rates of formation of *t*-C_{10} and *t*-C_4 were found to be 0.15 ± 0.0 mol olefin (mol catalyst)$^{-1}$ min^{-1}.

(16) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

(17) W. F. Edgell and C. H. Ward, *J. Am. Chem. Soc.*, **75**, 1169 (1953).

Thermal Decomposition of Labeled Cyclohexene. A Complex Reaction Involving a Forbidden 1,2-Hydrogen Elimination

D. C. Tardy,*[1a] R. Ireton,[1b] and A. S. Gordon[1c]

Contribution from the Chemistry Division, Naval Weapons Center, China Lake, California 93555. Received August 4, 1978

Abstract: The pyrolysis of 3,3,6,6-tetradeuteriocyclohexene is complex and involves four primary unimolecular processes (in a ratio of 20:1:0.1:0.02): retro-Diels–Alder ($\log k_1 = 14.93 \pm 0.79 - (65.2 \pm 2.8)/\theta$), D_2 elimination ($\log k_2 = 12.63 \pm 0.76 - (61.6 \pm 2.7)/\theta$), HD elimination, and H_2 elimination ($\theta = 2.303RT$ kcal/mol). The first two reactions are symmetry allowed. If the last two reactions are concerted, they are symmetry forbidden. The experimental activation energies for processes 3 and 4 are 6 ± 3 kcal/mol larger than that for process 2. Various mechanisms which may account for reactions 3 and 4 are discussed. Secondary reactions producing cyclohexadienes, benzene, H_2, and HD were also observed at low conversion (~2%); any D_2 produced by secondary processes was masked by reaction 2. The secondary reactions were initiated by reaction 9 with an activation energy of approximately 48 kcal/mol followed by reactions 10–16. Since the secondary rate of production of H_2 was much faster than reaction 4, the secondary production rate could be equated to the rate of formation of benzene from 1,3-cyclohexadiene.

Introduction

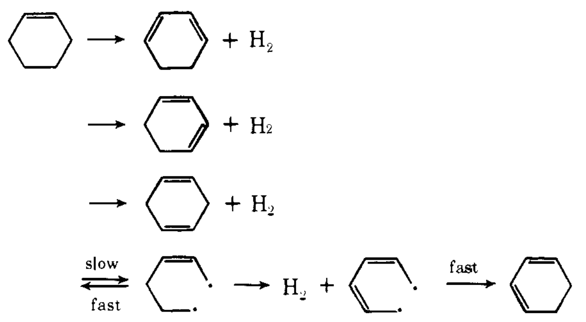
The gas-phase pyrolysis of cyclohexene[2,3] in the 400-850 °C temperature region produces primarily ethylene and 1,3-butadiene by a retro-Diels–Alder reaction. This reaction has been shown to be homogeneous, first order and is allowed by orbital symmetry; thus, a concerted Woodward–Hoffmann[4] process has been postulated. Along with ethylene and 1,3-butadiene small amounts (~5%) of hydrogen and 1,3-cyclohexadiene are observed.[2d] Presumably, these products, also formed by a homogeneous competitive first-order path,[2d] result from the molecular elimination of hydrogen.

$$\longrightarrow \mathrm{C{=}C + C{=}C{-}C{=}C} \qquad (1')$$

The production of molecular hydrogen via primary unimolecular processes could be by one or more of the following paths.

Process 2′ is a simple 1,4-elimination which is allowed by

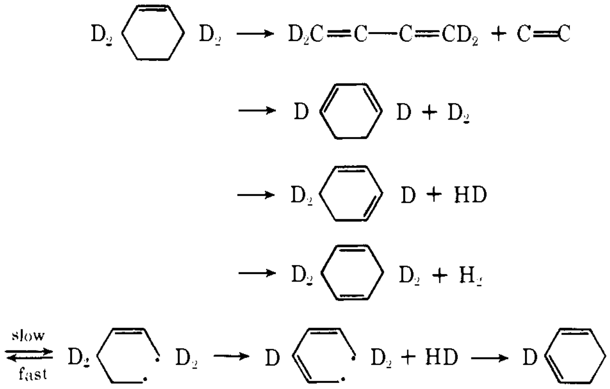
0002-7863/79/1501-1508$01.00/0



(2′)
(3′)
(4′)
(5′)

orbital symmetry, while the third and fourth processes (1,2-eliminations) are symmetry forbidden and thus are expected to have a somewhat higher critical energy for reaction (an activation energy which is approximately 15 kcal/mol[5,6] higher than process 2′). Owing to the steric requirements these three concerted processes (2′-4′) are expected to have *A* factors (related to the tightness of the transition state) which are less than 10-100 that for normal unimolecular reactions ($\sim 10^{14}$ s^{-1}). Process 5′, involving a bond fission followed by secondary processes, is difficult to analyze for *A* and *E* factors. The H_2 elimination in (5′) has been previously postulated by Gordon and Smith[7] and Stein and Rabinovitch.[8]

The present research was undertaken to provide an understanding at the molecular level of the processes which are involved in the thermal decomposition of cyclohexene. The relative importance of these paths can be determined by following the production of isotopically labeled products, including hydrogens, in the pyrolysis of 3,3,6,6-tetradeuteriocyclohexene (TDC) as a function of temperature, time, and pressure. The reactions for TDC, analogous to reactions 1′-5′ above, are



(1)
(2)
(3)
(4)
(5)

Apparatus, Material, and Procedure

TDC was obtained from Merck Sharp and Dohme, Ltd., Canada, and was purified gas chromatographically. The isotopic deuterium purity determined by mass spectrometry was 99+%; ^1H NMR showed that at least 99.4% of the 3 and 6 positions were labeled with deuterium. Dissolved gases were removed by the conventional freeze-pump-melt procedure.

Cylindrical quartz reaction vessels of about 115 cm^3 with surface to volume ratios of 1.25 and 10.06 cm^{-1} were each equipped with a small freeze-out side arm for introduction of samples into the reactors. A known amount of TDC was frozen into the side arm, pumped to 10^{-5} Torr, isolated from the system, gasified, and warmed to 60 °C before admittance into the previously evacuated reaction vessel. The dead volume was never more than 1.5% of the reactor volume.

The reaction was quenched by allowing the condensable products to freeze out on a silica-packed, 5-cm^3 Pyrex U-trap at 77 K. Noncondensable products (H_2, HD, and D_2) were expanded through the 5-cm^3 U-trap into a second 110-cm^3 U-trap at 77 K. After 10 min was allowed for diffusional equilibrium to be assured, the traps were sealed off with a torch (blanks consisting of H_2 and D_2 indicated that HD was not produced in the sealing procedure). The liquid nitrogen condensable products were analyzed chromatographically with a 25% 1-methyl-5-(2-methoxyethyl)tetrazole on C-22 firebrick-packed column (6 mm o.d. × 2 m) using a thermal conductivity detector. The cyclohexadiene component of the reaction mixture was separated on the column and trapped for subsequent analysis of deuterium content via the mass spectrometer. The noncondensable H_2, HD, and D_2 product distribution, as well as absolute molar amounts, was determined mass spectrometrically against a calibration mix of known H_2:HD:D_2 concentrations using the same procedure as in the above experiments. Quantitative values from the gas chromatograph runs were obtained by measurement of the peak area, with the sensitivities (peak area/mol) determined from calibration mixes run under normal column conditions.

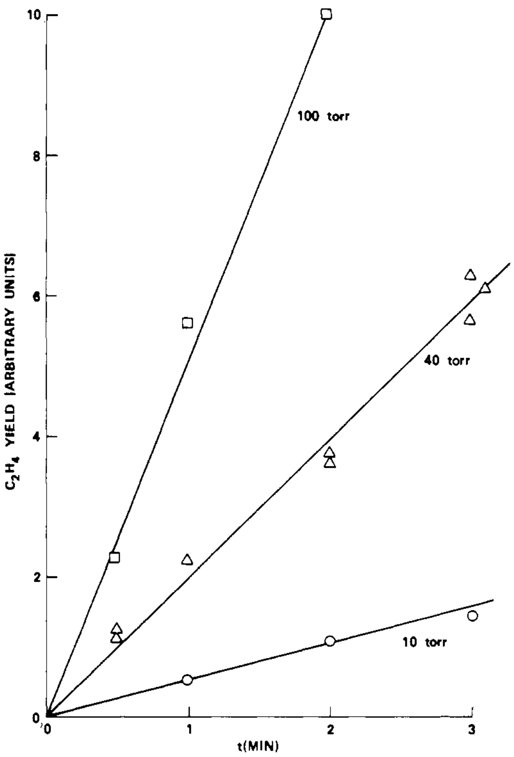


Figure 1. Plots of C_2H_4 yield (arbitrary units) vs. time at 500 °C for TDC pressures of: 10 Torr, ○; 40 Torr, △; 100 Torr, □.

The reactions were run for various times ranging from 0.5 to 10 min at three pressures (10, 40, and 100 Torr), measured with a Wallace Tiernan gauge at three temperatures (477, 500, and 525 °C). The maximum extent of reaction ranged from 4% at 477 °C up to 12% at 525 °C.

Results

As shown in Figure 1, the production of ethylene was linear with time for a given temperature and pressure. At constant temperature the ethylene production rate was proportional to pressure of TDC. The ethylene yield was also found to be independent of the reaction vessel's surface to volume ratio (S/V of 10.04 and 1.25 cm^{-1}). The addition of ethylene or 1,3-butadiene (5-25%) did not affect the production of ethylene. Thus, the ethylene production reaction was found to be homogeneous and unimolecular (in the pressure independent region) with a rate constant given by

$$\log k_1 = 14.93 \pm 0.79 - \frac{65.2 \pm 2.8}{\theta}$$

where $\theta = 2.303RT$ kcal/mol and the uncertainty is for one standard deviation. This value is in excellent agreement with the value of

$$\log k_1 = 15.16 - \frac{66.2}{\theta}$$

reported by Uchiyama, Tomioka, and Amano[3] in a flow system. The Arrhenius parameters obtained by Smith and Gordon

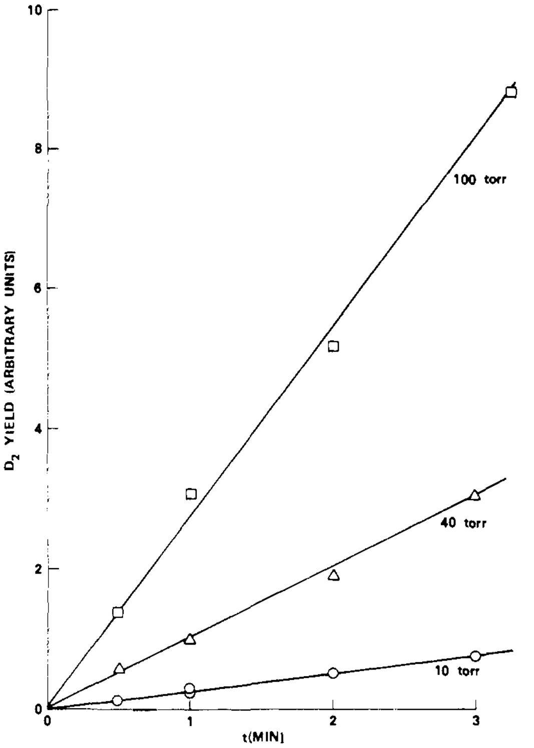


Figure 2. Plots of D_2 yield (arbitrary units) vs. time at 500 °C for TDC pressures of: 10 Torr, ○; 40 Torr, △; 100 Torr, □.

$(SG)^{2d}$ of this laboratory (their method consisted of inserting a Pyrex reaction vessel into a molten salt bath for a given time, followed by rapid cooling) is in disagreement with the above values; however, their absolute rate constants in the middle of the temperature range agree with the present study.

The production of D_2 was also linear with time for a given temperature and pressure (Figure 2). The D_2 production rate (approximately 0.05 of the ethylene rate) was independent of S/V, ethylene, or 1,3-butadiene (5-25%), and linearly dependent on the TDC pressure. Thus the D_2 reaction is homogeneous and unimolecular (in the pressure-independent region) with a rate constant given by

$$\log k_2 = 12.63 \pm 0.76 - \frac{61.6 \pm 2.7}{\theta}$$

which is not in agreement with

$$\log k_2 = 16.28 - \frac{71.2}{\theta}$$

reported by SG.[2d] The rate constants determined by SG[2d] at 500 °C are an order of magnitude larger than the ones reported here; this may be due to the small percent reaction carried out in the present study. The dideuterio-1,3-cyclohexadiene (2DC) yield parallels the D_2 yield such that

$$\log k_{2DC} = 13.44 \pm 0.60 - \frac{64.8 \pm 2.1}{\theta}$$

Within experimental error (~8%), the rate constants for D_2 and 2DC production are equal.

The experimental evidence firmly supports reactions 1 and 2; the production of ethylene from a diradical source (i.e., reaction 5) can be discarded from the observed low value of E_a (1). The presence of H_2, HD, and trideuterio-1,3-cyclohexadiene (3DC) and tetradeuterio-1,4-cyclohexadiene (4DC) requires that reactions 3-5 and/or others are operative. For a 2-min run at 500 °C, corresponding to 2% reaction, the total amount of H_2 and HD is approximately 0.2 of the observed D_2 yield or 0.01 of the ethylene yield; consequently, these "additional" reactions are not significant to the gross decomposition, but an understanding of their formation is necessary for a description of the overall decomposition process.

The HD and H_2 yields are not affected by the addition of ethylene; however, the addition of 1,3-cyclohexadiene (5-25%) increases these yields. Addition of 1,3-butadiene increases only the yield of HD. When the reaction is accelerated, both dienes have approximately the same efficiency on a per mol basis; since 1,3-butadiene is a much more prominent product than 1,3-cyclohexadiene it dominates the secondary hydrogen producing reactions. It is noted that the HD and H_2 yields increase with time in a nonlinear fashion. Increasing the S/V ratio also increases the yield of H_2 slightly while increasing the HD and 3DC to a smaller degree. Analysis of the results from the small and large S/V vessels indicates that the hydrogen rates are not appreciably surface dependent in the small S/V vessel. Since D_2 has been shown to be first order and homogeneous the effect of surface, secondary reactions, and reaction orders are best exhibited by plotting yield ratios (HD/D_2 and H_2/D_2) vs. time (i.e., to obtain correlations with a known homogeneous first-order process for D_2 production) for the various temperatures, pressures, and S/V studied. A summary of these plots is shown in Figure 3; Tables I-III contain the least-squares analyses of the experimental data. It is of particular interest that all the HD/D_2 and H_2/D_2 lines extrapolated to zero time have intercepts of 0.12 ± 0.03 and 0.03 ± 0.01, respectively, showing a first-order dependence on TDC component for the formation of HD and H_2. Also of interest is the nonzero slope, indicating that some HD and H_2 are produced by secondary reactions. If the slopes of these curves are plotted vs. pressure of TDC a straight line with nonzero intercept results, indicating that there are two secondary reactions—one with a greater than first order and the other a first order dependence on TDC. That is, the products from TDC can react both in a first-order reaction as well as a non-first-order reaction with the parent TDC.

The formation of HD also results in the production of 3DC (mass 83) while analogously 2DC (mass 82) is produced with D_2. Thus the mass 83/mass 82 ratio is expected to parallel the HD/D_2 plots. The breakdown of 3DC in the mass spectrometer produces a mass 82 peak; likewise 2DC will have the natural ^{13}C abundance and thus produce a mass 83 peak. The data are corrected for these patterns.

The 83/82 ratio increases more rapidly than the HD/D_2 ratio by a factor of approximately 2.5 as time increases (see Figure 3); however, the intercepts at $t = 0$ are the same within experimental error as those of the HD/D_2 plots. Likewise, the 84/82 ratio (mass 84 resulting from 4DC) parallels the H_2/D_2 ratio but has an intercept slightly less than that for H_2/D_2 at zero time.

The addition of light cyclohexene increases the H_2/D_2 ratio as expected (since H_2 is the sole elimination product from light cyclohexene) while the HD/D_2 and 83/82 ratios remain the same. Adding 1,3-butadiene or 1,3-cyclohexadiene increases the 83/82 ratio while addition of ethylene does not affect the 83/82 ratio.

Benzene and methylcyclopentane products were also observed. The benzene was considered a minor product, comparable to H_2. Since benzene is known to result from the pyrolysis of 1,3-cyclohexadiene some experiments using 5 Torr of 1,3-cyclohexadiene were carried out at 481 °C in a low surface reactor. Reaction time ranged from 6 to 30 min. At this pressure approximately 0.6% of the 1,3-cyclohexadiene reacted per min to produce benzene. Using this rate and the average amount of 1,3-cyclohexadiene formed in the TDC pyrolysis, good agreement was obtained between the actual amount of benzene and that which would be predicted. Thus it appears that the major source of benzene in the TDC pyrolysis is the decomposition of the 1,3-cyclohexadiene. Alfassi, Benson, and

Table I. Derived Intercepts from Yield Ratio vs. Time Plots[a]

	Torr	477 °C	500 °C	523 °C
H_2/D_2	10	0.072 ± 0.008^{16}	0.069 ± 0.003^{4}	0.042 ± 0.005^{10}
	40	0.036 ± 0.007^{11}	0.043 ± 0.003^{4}	0.054 ± 0.004^{12}
	100	0.031 ± 0.015^{11}	0.031 ± 0.004^{4}	0.055 ± 0.018^{7}
HD/D_2	10	0.137 ± 0.014^{16}	0.113 ± 0.004^{4}	0.106 ± 0.013^{10}
	40	0.124 ± 0.013^{11}	0.101 ± 0.010^{4}	0.147 ± 0.011^{12}
	100	0.106 ± 0.032^{11}	0.109 ± 0.012^{4}	0.153 ± 0.022^{7}
83/82	10	0.195 ± 0.033^{15}	0.117 ± 0.022^{4}	0.153 ± 0.017^{6}
	40	0.199 ± 0.05^{12}	0.097 ± 0.031^{7}	0.187 ± 0.017^{10}
	100	0.179 ± 0.087^{8}	0.175 ± 0.038^{4}	0.299 ± 0.082^{5}

[a] Superscript indicates the number of data points used in the least-squares analysis.

Table II. Derived Slopes from Yield Ratio vs. Time Plots[a]

	Torr	477 °C	500 °C	523 °C
H_2/D_2	10	-0.001 ± 0.001^{16}	0.003 ± 0.001^{4}	0.019 ± 0.004^{10}
	40	0.006 ± 0.001^{11}	0.016 ± 0.002^{4}	0.040 ± 0.005^{12}
	100	0.008 ± 0.002^{11}	0.032 ± 0.002^{4}	0.054 ± 0.017^{7}
HD/D_2	10	0.002 ± 0.002^{16}	0.023 ± 0.002^{4}	0.041 ± 0.012^{10}
	40	0.013 ± 0.002^{11}	0.043 ± 0.005^{4}	0.094 ± 0.012^{12}
	100	0.020 ± 0.005^{11}	0.074 ± 0.006^{4}	0.136 ± 0.022^{7}
83/82	10	0.008 ± 0.006^{15}	0.040 ± 0.012^{4}	0.068 ± 0.015^{6}
	40	0.023 ± 0.007^{12}	0.101 ± 0.016^{7}	0.210 ± 0.019^{10}
	100	0.045 ± 0.013^{8}	0.150 ± 0.020^{4}	0.249 ± 0.065^{5}

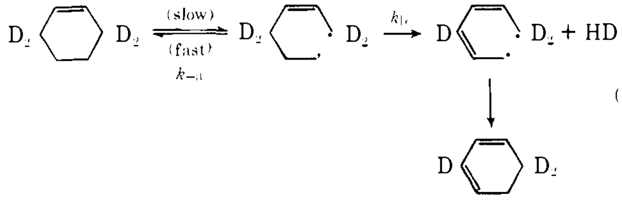
[a] Superscript indicates the number of data points used in the least-squares analysis.

Golden[6] have suggested that this decomposition can either be a biradical intermediate or a 1,2-symmetry forbidden mechanism. Our results show that for 2% reaction of TDC the benzene/2DC ratio is approximately equal to the H_2/D_2 ratio.

Discussion

Despite the experimental errors involved when observing minor products from a chemical reaction we conclude from the experimental results that both H_2 and HD are formed by primary homogeneous unimolecular processes with respect to TDC and two secondary reactions, the most important being second order with respect to TDC. As has been noted above there is also a minor secondary reaction which is first order. The two components will be discussed separately.

Primary Reactions. Both HD and H_2 are primary products since the HD/D_2 and H_2/D_2 vs. time plots give a nonzero value when extrapolated to zero time (0.12 and 0.03, respectively). The intercepts are, within experimental error, independent of pressure, indicating that the primary process is first order, since the reference reaction producing D_2 is first order with respect to TDC. The ratios increase slightly (on the order of 30%) as the temperature is increased from 477 to 525 °C. This increase corresponds to an activation energy difference of 6 ± 3 kcal/mol. Using the activation energy for D_2 production as 61.6 kcal/mol the HD and H_2 processes would have activation energies (E_a (HD) and E_a (H_2)) of approximately 68 ± 3 kcal/mol. With this result three mechanisms will be considered: first, the carbon–carbon bond rupture in TDC followed by elimination of HD and then ring closure (eq A). The rate of HD production for this mechanism is given by



(A)

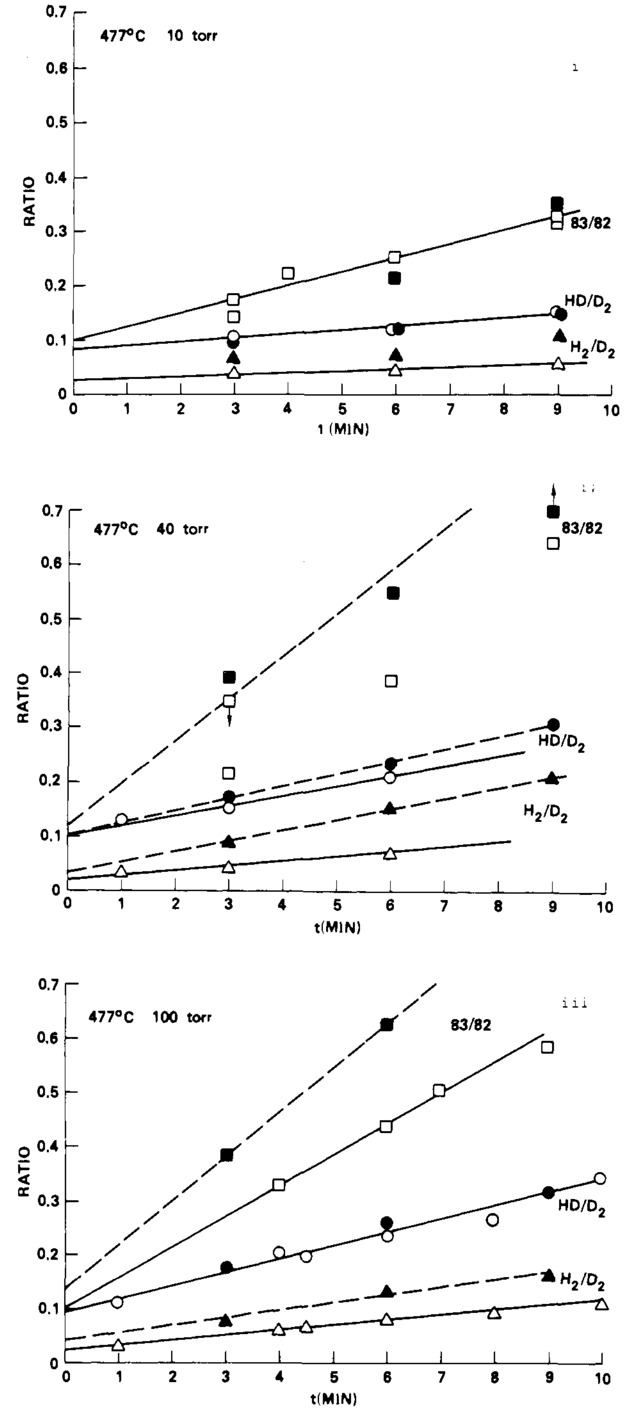


Figure 3. Plots of yield ratios vs. time for (i) 10 mm TDC, 477 °C; (ii) 40 mm TDC, 477 °C; (iii) 100 mm TDC, 477 °C. Open symbols are for S/V = 1.25 cm^{-1} and filled symbols for S/V = 10.06 cm^{-1}: △, H_2/D_2; ○, HD/D_2; □, 83/82.

$$\frac{d(HD)}{dt} = k_b \frac{k_a[TDC]}{k_{-a} + k_b} \approx k_b K_{eq}[TDC]$$

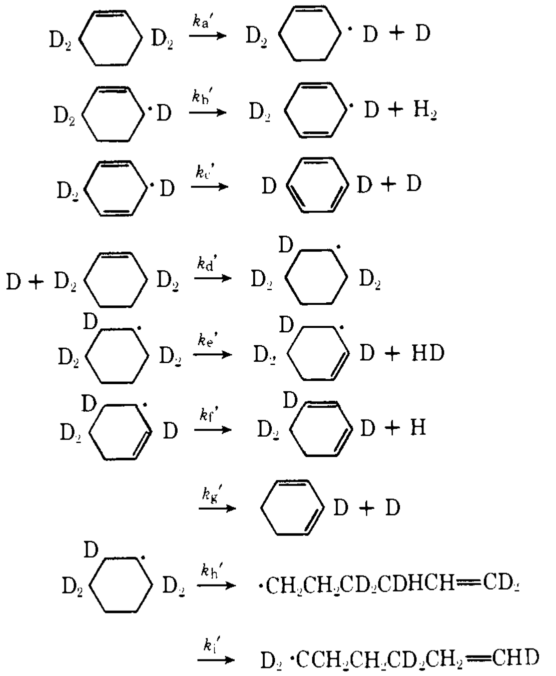
since $k_{-a} \gg k_b$. The temperature dependence of HD production for this sequence of reactions is $E_a(a) - E_a(-a) + E_a(b)$. Reaction b is expected to have an activation energy of at least 10 kcal/mol;[7] this value coupled with the allyl C-C bond energy (~70 kcal/mol)[9] and $E_a(-a)$ between 0 and 3 kcal/mol predicts an E_a(HD) in excess of 77 kcal/mol. In addition to giving an E_a(HD) approximately 9 kcal/mol higher than is observed, H_2 could not logically be formed by this mechanism.

Table III. Effect of S/V on Yield Ratio vs. Time Plots at 477 °C[a]

		intercept		slope	
	Torr	LSV	HSV	LSV	HSV
H_2/D_2	10	0.072 ± 0.008^{16}	0.047 ± 0.010^{3}	-0.001 ± 0.001^{16}	0.007 ± 0.002^{3}
	40	0.036 ± 0.007^{11}	0.052 ± 0.016^{4}	0.006 ± 0.001^{11}	0.017 ± 0.003^{4}
	100	0.031 ± 0.015^{11}	0.040 ± 0.020^{3}	0.008 ± 0.002^{11}	0.015 ± 0.003^{3}
HD/D_2	10	0.137 ± 0.014^{16}	0.062 ± 0.004^{3}	0.002 ± 0.002^{16}	0.010 ± 0.001^{3}
	40	0.124 ± 0.013^{11}	0.124 ± 0.019^{4}	0.013 ± 0.002^{11}	0.020 ± 0.003^{4}
	100	0.106 ± 0.032^{11}	0.112 ± 0.019^{3}	0.020 ± 0.005^{11}	0.023 ± 0.003^{3}
83/82	10	0.195 ± 0.033^{15}	-0.032^{2}	0.008 ± 0.006^{15}	0.038^{2}
	40	0.199 ± 0.05^{12}	0.194 ± 0.043^{4}	0.023 ± 0.007^{12}	0.052 ± 0.007^{4}
	100	0.179 ± 0.087^{8}	0.163 ± 0.019^{3}	0.045 ± 0.013^{8}	0.061 ± 0.003^{3}

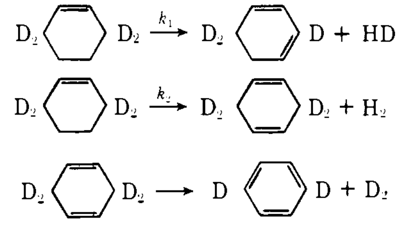
[a] Superscript indicates the number of data points used in the least-squares analysis.

Scheme I



The second possibility is that a chain process (Scheme I) is involved in which the initial step is the carbon-hydrogen bond rupture in TDC. Additional reactions involving H addition to TDC and subsequent elimination reactions ($\sim k_e'$) could be incorporated. This mechanism does account for *both* H_2 and HD formation; however, $E_a(\text{HD})$ ($= E_a(\text{a}') + E_a(\text{e}') - E_a(\text{h}',\text{i}')$) would be in excess of 80 kcal/mol since $E_a(\text{a}')$ is at least 80 kcal/mol[9] and $E_a(\text{e}')$ is greater than $E_a(\text{h}',\text{i}')$.[7,8]

The third alternative is the symmetry-forbidden 1,2 molecular elimination (eq 3 and 4). At these temperatures the 1,4-cyclohexadiene (reaction 4) gives benzene[10] (eq B) which



(3)

(4)

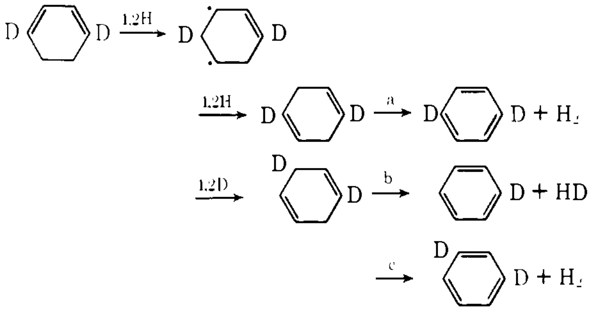
(B)

is observed at high percent conversion. However, the method of analytical analysis did not provide the sensitivity to determine the benzene as a function of time. (It will be shown later that benzene is also a product from a secondary reaction.) The mechanism above is in accord with the observation that the 84/82 ratio vs. time has an intercept with a value close to zero and definitely less than the H_2/D_2 intercept. The fact that HD is about 4-5 times the H_2 can be understood if reaction 4 has an activation energy greater than that for reaction 3; a 1,3-diene has a 4 kcal/mol stabilization energy. If all of the stabilization energy is in the transition state,[11] this would give HD rate enhancement of approximately 11 at 500 °C. However, an isotope effect of 2^{12} at this temperature would reduce the HD/H_2 ratio to between 5 and 6. Thus the HD/H_2 ratio is in accord with the molecular elimination mechanism.

The 1,2 molecular elimination of hydrogen from cyclopentene has been reported by Baldwin.[13] By using 4-deuteriocyclopentene and observing the d_1 and d_0 cyclopentadienes he concludes that the 1,4-elimination is approximately 12 times greater than the 1,2-elimination at 550 °C. Unfortunately, temperature studies were not performed so an activation energy could not be obtained. Nevertheless the value of 6, when correction for reaction path degeneracy is made, is in semiquantitative agreement with our value of 8-10 at a somewhat lower temperature. The 1,4 molecular elimination of hydrogen in cyclopentene has an activation energy of 61 kcal/mol and an A factor of $10^{13.35}$ (ref 14). These values are comparable to those observed in this work for TDC. Other investigators have shown that in activation energy the penalty for a forbidden reaction is equal to or greater than 15 kcal/mol.[5,6] This value is somewhat higher than we have determined but is within the large experimental error.

From the above possibilities our experimental data supports a 1,2 molecular elimination from TDC; unfortunately, the experimental errors are not small since extrapolation to eliminate secondary reactions is needed.

Secondary Reactions. Since the ratios H_2/D_2 and HD/D_2 (83/82 and 84/82) increase with time, H_2 and HD (mass 83 and 84) must be produced from the reaction of major primary products such as 1,3-butadiene-d_4, ethylene, and 1,3-cyclohexadiene-d_2. The increase of the H_2/D_2 ratio is the smallest and is less dependent upon pressure than the other. Since the amount of benzene (when measurable quantities of benzene are present) is approximately equal to that of H_2, the decomposition of 1,3-cyclohexadiene is important. Alfassi et al.[6] have concluded that the pyrolysis of 1,3-cyclohexadiene probably proceeds by a mechanism involving 1,2 hydrogen shifts. For 2DC reactions 6-8 would occur. Reactions a, b, and c are rapid



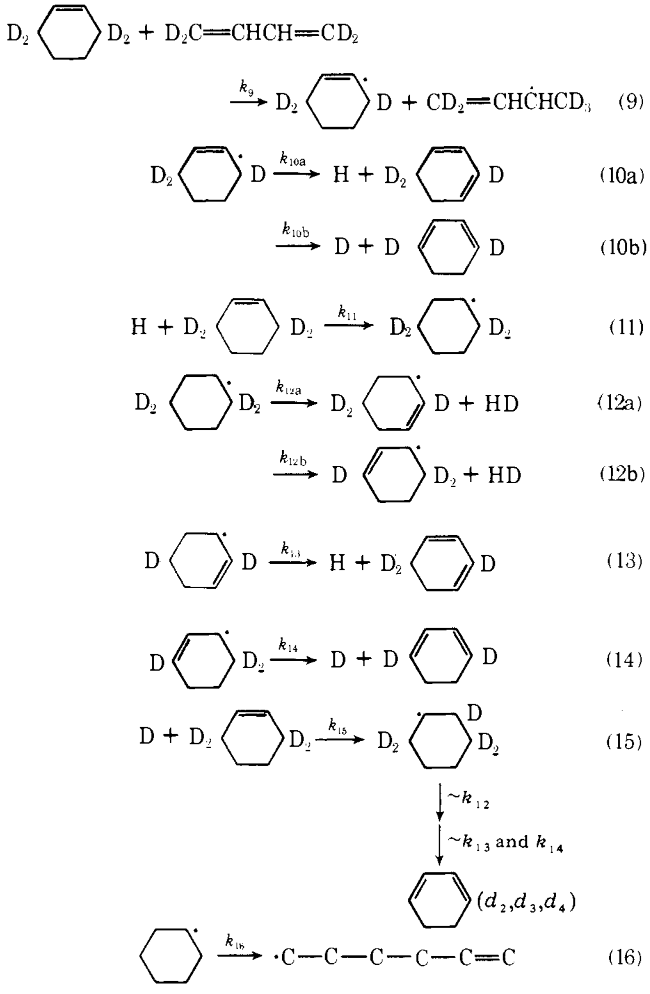
(6)

(7)

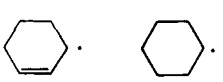
(8)

in this temperature region[10] so 1,4-cyclohexadiene will not be present. If the isotope effect for migration is normal (no studies have been reported for analogous reactions) then H_2 will be 90% of the benzene produced. The temperature dependence of secondary H_2 yield produces an Arrhenius activation energy of 48 ± 15 kcal/mol, which is within the value of 59 kcal/mol reported by Alfassi et al.[6]

For a given exposure time, the HD/D_2 and 83/82 ratios depend on pressure; when the slopes of the HD/D_2 and 83/82 vs. time plots are plotted vs. pressure of TDC a nearly linear relation is observed. The intercept is somewhat larger than zero, indicating that a first-order process may be present. However, the dominant secondary reaction is second order with respect to TDC. The slopes show a temperature dependence of approximately 48 kcal/mol with the magnitude of the 83/82 slope approximately 2.5 times larger than the HD/D_2 slope. This is coupled with the fact that both 1,3-cyclohexadiene and 1,3-butadiene in separate experiments have been shown to increase the 83/82 and HD/D_2 ratio roughly the same for equal concentrations, and that 1,3-butadiene is in a 20-fold excess of 1,3-cyclohexadiene. Reactions 9–16 are proposed.



Assuming a steady state for i, ii, and H, the HD/D_2 and 82/82 ratios are



i ii

$$\frac{HD}{D_2} = k_9 \frac{k_{12}}{k_{16}} \frac{k_1}{k_2} [TDC]t$$

$$\frac{83}{82} = k_9 \frac{k_{12}}{k_{16}} \frac{k_1}{k_2} \left(1 + \frac{k_{16}}{k_{12}}\right) [TDC]t = \frac{HD}{D_2} \left(1 + \frac{k_{16}}{k_{12}}\right)$$

Since 83/82 is 2.5 times HD/D_2, k_{16}/k_{12} would be approximately 1.5. From the experimental data at 500 °C, HD (secondary)/D_2 = 0.1, and since E_{12} is approximately equal to E_{16} and E_{14} is approximately equal to E_2

$$k_9 = 10^{10\pm3}\, 10^{-48\pm10/\theta} \frac{\text{cm}^3}{\text{mol·s}}$$

This value can be compared with the analogous reaction reported by Back et al.:[15]

$$H_2C{=}CH_2 + H_2C{=}CH_2 \rightarrow H_2C{=}\dot{C}H + H_3C{-}\dot{C}H_2 \quad (17)$$

where $k_{17} = 10^{14.8} \times 10^{-65/\theta}$ cm^3/mol·s. Within experimental error the A factors are comparable; however, the difference in E factors is probably due to the stabilization (~13 kcal/mol)[9] provided by the allyl-type structure of i and $C{=}C{-}\dot{C}{-}C$.

This mechanism accounts for all the experimental observations and approximates the accepted A and E factors for analogous reactions. Other mechanisms were considered, ranging from a direct bimolecular reaction between TDC and 1,3-butadiene to give HD and 1,3-cyclohexadiene directly (this was not only deficient in the A factor but the HD/D_2 and 83/82 ratios were equal). The proposed mechanisms were assessed by changing the termination step (reaction 16); if termination was a bimolecular combination of two ii or two i, there was no pressure dependence for the HD/D_2 and 83/82 ratios, and the time dependency was $t^{1/2}$. If a bimolecular termination involving either ii or i were used the proper time dependence was obtained but there was no dependence on TDC pressure.

Summary

The thermal decomposition of TDC is complex and involves at least four primary unimolecular processes (retro-Diels-Alder (~95%), D_2 elimination (~5%), HD elimination, and H_2 elimination (~0.5%)). The latter two processes are symmetry forbidden and have an activation energy approximately 6 kcal/mol larger than the symmetry-allowed elimination of D_2 ($E_a(D_2) \approx 65.2$ kcal/mol). Secondary reactions producing cyclohexadienes, benzene, H_2, and HD were also observed at low conversion. The secondary reactions (~2%) appear to be initiated by a D transfer from TDC to a 1,3-diene (most likely 1,3-butadiene or 1,3-cyclohexadiene).

Acknowledgments. D.C.T. wishes to thank the Naval Weapons Center (NWC) for supplying the scientific environment and Visiting Research Scientist position for the year in which these experiments were performed. Likewise R.I. appreciates a postdoctoral position at NWC. Computing funds from the University of Iowa Graduate College for data analysis were greatly appreciated.

Supplementary Material Available: A table of summary data for the pyrolysis of TDC, the method used for the mass 82 correction, and plots of the yield ratios at 500 and 523 °C (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Department of Chemistry, University of Iowa, Iowa City, Iowa 52242; (b) Naval Weapons Center; (c) Department of AMES, University of California, San Diego, Calif. 92037.
(2) (a) L. Kuchler, *Nachr. Ges. Wiss. Goettingen*, 1, 231 (1939); (b) M. Kraus, M. Varuska, and V. Bazant, *Collect. Czech. Chem. Commun.*, **22**, 484 (1957); (c) W. Tsang, *J. Chem. Phys.*, **42**, 1805 (1961); (d) S. R. Smith and Alvin S. Gordon, *J. Phys. Chem.*, **65**, 1125 (1961).
(3) Masao Uchiyama, Tadao Tomioka, and Akira Amano, *J. Phys. Chem.*, **68**, 1878 (1964).
(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(5) (a) J. I. Brauman and W. C. Archie, Jr., *J. Am. Chem. Soc.*, **94**, 4262 (1972); (b) J. I. Brauman and D. M. Golden, *ibid.*, **90**, 1920 (1968); (c) D. M. Golden

and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).
(6) Zeev B. Alfassi, Sidney W. Benson, and David M. Golden, *J. Am. Chem. Soc.*, **95**, 4784 (1973).
(7) (a) A. S. Gordon and S. R. Smith, *J. Chem. Phys.*, **34**, 331 (1961); (b) *J. Phys. Chem.*, **66**, 521 (1962).
(8) S. E. Stein and B. S. Rabinovitch, *J. Phys. Chem.*, **79**, 191 (1975).
(9) (a) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970.
(10) (a) R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966); (b) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 985 (1967).
(11) D. C. Tardy, *J. Am. Chem. Soc.*, **97**, 5695 (1975).
(12) D. C. Tardy, A. S. Gordon and W. P. Norris, *J. Phys. Chem.*, **80**, 1398 (1976).
(13) John E. Baldwin, *Tetrahedron Lett.*, 2953 (1966).
(14) K. D. King, *Int. J. Chem. Kinet.*, **10**, 117 (1978).
(15) (a) M. L. Boyd, T. M. Wu, and M. H. Back, *Can. J. Chem.*, **46**, 2415 (1968); (b) M. L. Boyd and M. H. Back, *ibid.*, **46**, 2427 (1968).

Synthesis and Reactivity of Coordinated Imines Derived from 2-Keto Acids

J. MacB. Harrowfield and A. M. Sargeson*

Contribution from the Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia 2600.

Received May 26, 1978

Abstract: The synthesis of a series of $[Co(NH_3)_5OCOCOR]^{2+}$ ions (R = H, CH_3, C_6H_5, COOH, $-CH_2C_6H_5$, $C(CH_3)_3$, $CH_2CH_2CO_2^-$) and a number of derivatives is described. In aqueous base most of these ions undergo cyclization to tetraammine iminocarboxylato chelates which undergo a variety of reactions: alkylation of the deprotonated imine N center, addition of nucleophiles at the imine C center, reduction of the imine to give an amino acid, and intramolecular condensations after the addition of the nucleophile. The compounds illustrate the potential of the metal ion to protect and activate organic molecules as well as to organize such intramolecular condensations. The kinetics of the imine cyclization are also discussed.

Introduction

The imine functional group, >C=N–, plays a near-ubiquitous role in synthetic organic, biological, and coordination chemistry. Nonetheless, while there is a vast literature concerning the effects of Schiff base ligands on metal ion properties, only for complexes of Schiff bases derived from pyridoxal has there been any systematic and thorough investigation of the properties of imine containing ligands as affected by a metal ion.[1] The reactivity of simple coordinated imines is essentially unknown. Further, while an extremely large number of so-called "template" reactions[2] involve imine formation, no detailed study of the kinetics of genuine intramolecular condensations is available. It might well be anticipated from the behavior of related systems[3] that the (carbinolamine) addition intermediate involved in imine formation would be stabilized by metal ion coordination and that the kinetics of its formation and decomposition would therefore be amenable to investigation. It is frequently difficult to detect and therefore to understand factors controlling the stability of carbinolamine intermediates in simple organic systems.[4] In preliminary publications[5] we have outlined the synthesis and some aspects of the chemistry of simple cobalt(III) imine complexes and in related work detailed studies of the kinetics of genuine intramolecular imine formation with cobalt(III) have been made.[6] The present work describes the synthesis, formation kinetics and basic physical and chemical properties of a variety of α-iminocarboxylate complexes of cobalt(III).

Experimental Section

pH measurements were made under nitrogen at 25 °C using a Radiometer PHM26 meter with G202B glass electrode. Infrared spectra of KBr disk, Nujol mull (NaCl plates), and solution (D_2O, CaF_2 cell) samples were recorded with a Perkin-Elmer Model 337 instrument. Visible spectra and slower reaction rates were measured with a Cary-Varian 118C UV-visible spectrophotometer while reaction rates corresponding to half-lives of <2 s were measured with a Durrum-Gibson stopped flow kinetics spectrophotometer. Separate solutions of complex in 1 M $NaClO_4$ and NaOH (plus $NaClO_4$ to an ionic strength of 1.0) were degassed under water pump vacuum prior to thermal equilibration in the reservoirs of the stopped-flow apparatus. NMR spectra were recorded with JEOL "Minimar" MH 100 (proton) and FX-60 (^{13}C) instruments using tetramethylsilane (Me_4Si) in dimethyl-d_6 sulfoxide (Me_2SO-d_6) and sodium trimethylsilylpropanesulfonate in D_2O as references for ^1H spectra and dioxane (in D_2O) for ^{13}C.

Syntheses. 1. α-Ketocarboxylatopentaamminecobalt(III) Complexes. Trimethylpyruvic acid,[7] phenylglyoxylic acid,[8] and phenylpyruvic acid[9] were prepared by literature methods. Glyoxylic acid (BDH), ketomalonic (mesoxalic) acid (Lights), sodium pyruvate (Sigma), and α-ketoglutaric acid (ROC-RIC) were commercial products, though disodium ketomalonate was also prepared by base hydrolysis of dibromomalonic acid.[10] $[(NH_3)_5CoO_2CCOCH_3](ClO_4)_2$, $[(NH_3)_5CoO_2C{\cdot}CHO](ClO_4)_2[(NH_3)_5CoO_2C{\cdot}CO{\cdot}C_6H_5][(ClO_4)_2$, and $[(NH_3)_5CoO_2C{\cdot}CO{\cdot}C(CH_3)_3](ClO_4)_2$ were prepared by reaction of $[(NH_3)_5CoOH_2]^{3+}$ in a buffer of the ligand following the general procedure of Taube and Price[11] (though a 90-min reaction period was found sufficient. Note that full characterization of only the glyoxylatopentamminecobalt(III) complex is reported therein. Data for the related new species[12] are given below.) Anal. Calcd for $[Co(NH_3)_5OCOCOCH_3](ClO_4)_2$: Co, 13.71; C, 8.38; H, 4.22; N, 16.29; Cl, 16.49. Found: Co, 13.91; C, 8.74; H, 4.63; N, 16.12; Cl, 16.31.

^{13}C NMR (NB. The generally low solubility of the α-ketocarboxylatopentaamminecobalt(III) complexes meant that ^{13}C NMR spectra could be conveniently obtained for only a few species.): Consistent with the known ^1H NMR spectrum,[11,12] the ^{13}C spectrum showed resonances attributable to both keto and *gem*-diol forms of the complex. Relative to dioxane in 10^{-3} M DCl: +1976 (>C=O), +1736 (CO_2H, hydrate form), +1576 (CO_2H, keto form), +394 ($>C(OH)_2$), −597 (CH_3, keto), −619 Hz (CH_3, hydrate) (assignments tentative).

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl): 500 nm, 71.5 M^{-1} cm^{-1}.

Anal. Calcd for $[Co(NH_3)_5OCOCOC_6H_5](ClO_4)_2$: Co, 11.98; C, 19.53; H, 4.10; N, 14.23; Cl, 14.41. Found: Co, 12.0; C, 19.6; H, 4.2; N, 14.1; Cl, 14.2.

^{13}C NMR: +2880 (>C=O), +2751 (CO_2H, approximately twice the intensity of the 2880-Hz resonance), +2148, 2087, 2068, 2053 Hz (C_6H_5 group) relative to dioxane in 10^{-3} M DCl.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl) 498 nm, 77.1 M^{-1} cm^{-1}.

Anal. Calcd for $[Co(NH_3)_5OCOCOC(CH_3)_3](ClO_4)_2$: Co, 12.48;

0002-7863/79/1501-1514$01.00/0