both cases the slow-exchange limit nmr parameters are held constant at the values J_{AB} = 67.5 Hz, δ_{AB} = 527 Hz, J_{AX} = 207 Hz, and J_{BX} = 142 Hz used in the previous section.

In this case the spectra using the exact method and the first-order approximation are almost indistinguishable for exchange rates up to 100 sec^{-1} for both basic set A (Figure 13) and basic set B (Figure 14). In an experimental situation, of course, the first-order approximation could only be relied on at those rates where the lines being used to obtain rate or mechanistic information remained well resolved, *i.e.*, up to about 25 sec^{-1} for the outer doublets associated with the axial ligands.

A comparison of Figures 13 and 14 with the observed spectrum shown in Figure 3 indicates that in this case reliable mechanistic information could be obtained from this approximation. In general, the better the resolution the more useful this "first-order" approximation will become.

Caution must be exercised in applying this approximation to systems with degenerate transitions.

Addition of a Coordinated Nucleophile to a Free Carbonyl Center. The Formation of Acetylacetonatobis(ethylenediamine)cobalt(III) Ion

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Abstract: The mechanism of formation of $[Co(en)_2acac]^{2+}$ from *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ and -$[Co(en)_2(OH)_2]^{+}$ and acetylacetone (acacH) is shown to occur by addition of the two coordinated oxygens to the two carbonyl centers of acetylacetone. Retention of configuration at Co(III) is implied and observed. Some reactant complex isomerization to *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ is detected along with $[Co(en)_2acac]^{2+}$ formation and reconversion to the cis form leads to formation of more $[Co(en)_2acac]^{2+}$ (racemate) as a secondary process. The isomerization and racemization of the hydroxoaqua species are also examined. From consideration of the limited data available on the oxygen exchange between acetylacetone and water, an estimate of the residual nucleophilicity of OH^- when coordinated to Co(III) is made.

The reaction between *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ (en = 1,2-diaminoethane) and 2,4-pentanedione (acetylacetone) to form $[Co(en)_2acac]^{2+}$ was first described by Werner.[1] Its rapidity has more recently been noted by Boucher and Bailar,[2] though some forcing is required to drive the reaction to completion.[3] While the diaqua and dihydroxo complexes have been studied rather thoroughly with respect to isomerization[4,5] and oxygen exchange[5] in water, rather less is known about the hydroxoaqua species. They are certainly more reactive than their protonated and deprotonated counterparts, but only one ^{18}O exchange measurement has been made where the hydroxoaqua concentration was reasonable[5] and the isomerization reactions also have only been studied in a desultory way.[5-7] This paper now examines the reaction between the hydroxoaqua ion and acetylacetone and also the interconversion of the cis and trans isomers and the racemization of the cis ion.

Experimental Section

Spectrophotometric measurements were made on Cary 14 and 16 instruments and rotations were determined for a 1-dm cell on a Perkin-Elmer P22 spectropolarimeter. Readings of pH were taken on a Radiometer pH meter with TTA_3 electrode assembly, and mass spectral measurements were made on AEI MS902 and Atlas M86 instruments.

Acetylacetone (Fluka, puriss) was dried over anhydrous Na_2SO_4 and fractionally distilled immediately prior to use. 2,4,6-Collidine was fractionally distilled prior to the preparation of buffers. All other chemicals were of analytical reagent grade. Cation exchange experiments were conducted with Bio-Rad Analytical Grade Dowex 50WX2 (200–400 mesh) resin.

Synthesis. *cis*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ was prepared by adjusting the pH of an ice-cold solution of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ to a value between 7 and 8 and allowing the complex to crystallize, essentially the procedure described by Kruse and Taube.[5] The trans isomer was obtained by recrystallizing this material from hot water. It was also prepared simply by adding 1 mol of $LiOH \cdot H_2O$ to a concentrated solution of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ at room temperature. Solutions of *cis*-$[Co(en)_2(OH_2)_2](ClO_4)_3$ were prepared by dissolving *cis*-$[Co(en)_2CO_3]ClO_4$ in a slight excess (5%) of $HClO_4$ (5 *M*) and heating until all CO_2 had been displaced.

Anal. Calcd for $CoC_4H_{19}N_4Cl_2O$: Co, 14.3; C, 11.6; H, 4.6; N, 13.6; Cl, 17.2. Found: (cis) Co, 14.3; C, 11.7; H, 4.8; N, 13.6; Cl, 17.2; (trans) Co, 14.2; C, 11.8; H, 4.6; N, 13.5; Cl, 17.1.

$[Co(en)_2acac]I_2 \cdot H_2O$. Finely ground *cis*-$[Co(en)_2(OH_2)OH]$-$(ClO_4)_2$ (2.0 g) was added to a solution of 2,4-pentanedione (0.5 g) in water (10 ml). The mixture was stirred for 15 min, then filtered and treated with excess NaI. Red crystals formed immediately and, after 15 min of cooling on ice, were collected and washed with ethanol and ether, yield 2.2 g (83%). The complex was recrystallized from water.

Anal. Calcd for $CoC_9H_{25}N_4O_3I_2$: Co, 10.71; C, 19.65; H, 4.58; N, 10.19; I, 46.14. Found: Co, 11.17; C, 19.64; H, 4.59; N, 10.17; I, 46.17.

Kinetics. All rate measurements were made at 25°. Measurements of the isomerization rates of the $[Co(en)_2(OH_2)OH]^{2+}$ ions at other temperatures have been made previously.[6]

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[2] L. J. Boucher and J. C. Bailar, Jr., *Inorg. Chem.*, 3, 589 (1964).

[3] I. K. Reid and A. M. Sargeson, *Inorg. Syn.*, **9**, 167 (1960).

[4] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 6, 1265 (1952).

[5] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, 83, 1280 (1961).

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(a) **Isomerization of *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$.** To cover the region where the hydroxoaqua species were the predominant forms, isomerization rates were measured over the pH range 4–9 using pyridine, collidine, and Tris buffers at ionic strengths of 0.25 and 1.00 *M*. Only at times longer than those required to reach isomeric equilibrium was there any evidence of the formation of buffer complexes or polynuclear species (from ion-exchange analysis of the reaction mixture components). Bjerrum and Rasmussen[8] have previously shown that the formation of polynuclear complexes from the hydroxoaqua species is slow and proceeds only to a limited extent. Rates were followed spectrophotometrically both at constant wavelength and using repetitive scans over the range 650–320 nm to demonstrate the isosbestic points for the single process. In this wavelength range, optical density changes were small except in the vicinity of 510 nm, and all constant wavelength scans were made at 510 or 500 nm. The approach to equilibrium was followed with both cis and trans reactants, at least duplicate runs being made with each. At the lower pH's the predominance of the cis isomer at equilibrium led to only very small optical density changes being observed with cis reactant and only runs with the trans isomer provided accurate measures of the rate of approach to equilibrium.

(b) **Loss of Optical Activity in *cis*-$[Co(en)_2(OH_2)OH]^{2+}$.** A solution of $(-)_{589}$-$[Co(en)_2(OH_2)_2]^{3+}$ was prepared by dissolution of $(-)_{589}$-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$ (0.5 g; $[\alpha]_{589} = -1340°$, 0.1% in H_2O) in excess $HClO_4$ (5 ml, 2 *M*). Carbon dioxide was removed by passing a rapid stream of nitrogen through the solution for 5 min. A portion of the solution (0.1 ml) was mixed with an aliquot (10 ml) of buffer as used in the isomerization measurements and the rate of loss of optical activity followed polarimetrically at 545 nm (a minimum for $(-)_{589}$-$[Co(en)_2(OH_2)OH]^{2+}$ [7]). The pH of the final reaction mixture was measured.

(c) **Formation of $[Co(en)_2acac]^{2+}$.** Reaction was followed spectrophotometrically at a constant wavelength, using stopped-flow procedures to achieve rapid mixing of reactants. As it is very difficult to ensure absolute isomeric purity of *cis*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ solid, the pure complex was more conveniently generated from *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ prepared in solution by dissolving $[Co(en)_2CO_3]ClO_4$ in $HClO_4$ (CO_2 being removed by N_2 flushing). The dilute acid solution then comprised one of the components mixed in the stopped-flow reactor. It should be noted that to obtain concentrated aqueous solutions of acetylacetone, relatively high concentrations of $NaClO_4$ were necessary. The solubility of acetylacetone in water is very much enhanced by the presence of electrolytes.[9] The final ionic strength of all reaction media was 1.00 and saturation concentration of acetylacetone was then $\lesssim 1.5$ *M*. Since, however, the saturation concentration of acetylacetone in 2 *M* $NaClO_4$ is >4 *M*, supersaturated solutions of concentrations of 1.5 and 2.0 *M* (at ionic strength 1.0) were readily prepared and were of sufficient stability for several half-lives of reaction to be followed at the pH of maximum rate. At only this pH the effect of varying the acetylacetone concentration was determined, and at all other pH's a constant concentration of 1.0 *M* was used. Above pH 7 acetylacetone itself provided adequate buffering of the reaction mixtures, but below this pH the use of dilute (0.05 *M*) pyridine and collidine buffers was necessary. Because the slow base catalyzed cleavage of acetylacetone produces spectral changes below 400 nm, absorbance changes in the visible region only were examined and most scans were made at 500 nm, a wavelength where there is a very large difference in extinction coefficients. All runs were made in triplicate at least.

Isotopic Labeling Experiments. *cis*-$[Co(en)_2(OH_2)_2](ClO_4)_3$ (0.5 g, a deliquescent red powder obtained by dissolving $[Co(en)_2CO_3]ClO_4$ in excess 70% $HClO_4$ and triturating the resultant oil with ether) was dissolved in enriched (5% ^{18}O) water containing a trace of $HClO_4$ and heated at 60° for 6 hr.[5] The water was removed by trap to trap distillation under high vacuum and the residue of complex was dissolved in buffer (5 ml) prepared from NaOH (1 *M*, 5 ml), acetylacetone (1.0 g), and water (5 ml). Reaction was allowed to proceed for 2.5 min at room temperature, then excess NaI was added and the solution cooled on ice for ~2 min before collecting the $[Co(en)_2acac]I_2 \cdot H_2O$ (0.4 g). To remove a little $[Co(en)_2(OH_2)OH]I_2$ contaminant, the solid was dissolved in methanol and filtered and the complex was recrystallized by the addition of ether. It was then dried under high vacuum for 24 hr. Under such conditions the water of crystallization is retained.

Anal. Calcd for $CoC_9H_{25}N_4O_3I_2$: C, 19.65; H, 4.58; N, 10.19; I, 46.14. Found: C, 19.77; H, 4.43; N, 10.22; I, 45.98.

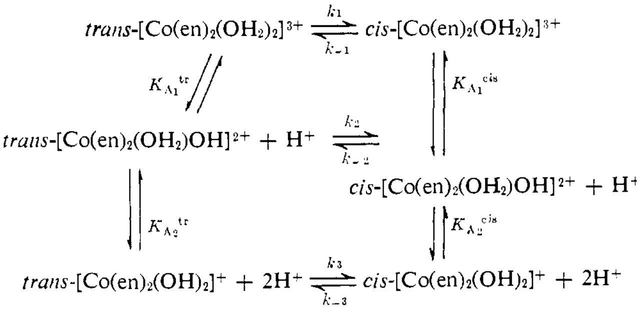
To obtain a crude estimate of the retention of label the complex was heated to 250° in the direct inlet probe of the MS9 mass spectrometer. Acetylacetone distilled off prior to ethylenediamine and the peak heights at mass numbers 100 and 102, the parent peaks, and mass numbers 43 and 45, corresponding to the acetylium ion, were measured. As a more sensitive procedure, the initial labeling of the diaqua comples was determined by equilibration of the recovered enriched water with normal CO_2 and the total oxygen isotope composition of the $[Co(en)_2acac]I_2 \cdot H_2O$ product was determined by pyrolysis with $Hg(CN)_2$–HgI_2 to give CO_2,[10] the *m/e* 46/44 ratio for both CO_2 samples being measured on the Atlas M86 ratio recording instrument. A normal CO_2 standard was also run.

Retention of Configuration in $[Co(en)_2acac]^{2+}$ Formation. As a simple index of the extent to which isomerization of reactant and formation of $[Co(en)_2acac]^{2+}$ were competitive, the optical purity of $[Co(en)_2acac]^{2+}$ generated from optically pure *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ was determined. (In essence, this experiment has been performed previously by Werner.[11]) For final acetylacetone concentrations of 0.25 and 1.0 *M*, reaction media were prepared exactly as for the kinetic runs except that $(-)_{589}$-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$ ($[\alpha]_{589} = -1340°$, 0.1% in H_2O) was used as a source of $(-)_{589}$-*cis*-$[Co(en)_2(OH_2)OH]^{2+}$. After 120 min of reaction the rotations were compared with those of optically pure $(-)_{589}$-$[Co(en)_2acac]I_2$[3] ($[\alpha]_{589} = -420°$, 0.1% in H_2O) dissolved in the same media. The reaction media pH was 7.1.

Results and Analysis

Isomerization and Racemization of $[Co(en)_2(OH_2)OH]^{2+}$. The data for isomerization of *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ and for loss of optical activity of $(-)_{589}$-*cis*-$[Co(en)_2(OH_2)OH]^{2+}$ were readily analyzed as reversible first-order reactions. Excellent linear rate plots of $\log |A_\infty - A_t|$ and $\log \alpha_t$ against time covering always more than three half-lives were obtained. Data for the rate of approach to isomerization equilibrium as a function of pH are given in Figure 1(a) for ionic strengths of 0.25 and 1.0 *M* and clearly the rates are insensitive to this variation. The plot shows a relatively sharp maximum in the neutral pH region, reflecting the greatly enhanced lability of the hydroxoaqua species relative to the diaqua and dihydroxo ions. Extraction of the individual iosmerization rate constants for the $[Co(en)_2(OH_2)OH]^{2+}$ complexes from these data requires knowledge of the isomeric equilibrium constants, isomerization rates, and acidity/basicity constants of the diaqua and dihydroxo complexes. For the reaction scheme (Scheme I) the observed rate of approach to isomeric equilibrium is given by

Scheme I



$$v = k_{\text{obsd}}[\text{Co}^{\text{III}}]$$

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[8] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 9, 735 (1955).

[9] H. Johansson and J. Rydberg, *Acta Chem. Scand.*, 23, 2797 (1969).

[10] M. Anbar and S. Guttman, *J. Appl. Rad. Isotopes*, 5, 233 (1959).

[11] A. Werner, J. Schwyzer, and W. Karrer, *Helv. Chim. Acta*, 4, 113 (1921).

where

$$k_{\mathrm{obsd}} = \frac{k_1[\mathrm{H}^+]^2 + k_2K_{\mathrm{A}_1}{}^{\mathrm{tr}}[\mathrm{H}^+] + k_3K_{\mathrm{A}_1}{}^{\mathrm{tr}}K_{\mathrm{A}_2}{}^{\mathrm{tr}}}{[\mathrm{H}^+]^2 + K_{\mathrm{A}_1}{}^{\mathrm{tr}}[\mathrm{H}^+] + K_{\mathrm{A}_1}{}^{\mathrm{tr}}K_{\mathrm{A}_2}{}^{\mathrm{tr}}} + \frac{k_{-1}[\mathrm{H}^+]^2 + k_{-2}K_{\mathrm{A}_1}{}^{\mathrm{cis}}[\mathrm{H}^+] + k_{-3}K_{\mathrm{A}_1}{}^{\mathrm{cis}}K_{\mathrm{A}_2}{}^{\mathrm{cis}}}{[\mathrm{H}^+]^2 + K_{\mathrm{A}_1}{}^{\mathrm{cis}}[\mathrm{H}^+] + K_{\mathrm{A}_1}{}^{\mathrm{cis}}K_{\mathrm{A}_2}{}^{\mathrm{cis}}}$$

Literature values for all constants other than k_2 and k_{-2} are available, and the full curve shown in Figure 1(a) represents the calculated values of k_{obsd} for $K_{\mathrm{A}_1}{}^{\mathrm{tr}} = 3.55 \times 10^{-5}$,[4] $K_{\mathrm{A}_2}{}^{\mathrm{tr}} = 1.15 \times 10^{-8}$,[4] $K_{\mathrm{A}_1}{}^{\mathrm{cis}} = 8.71 \times 10^{-7}$,[4] $K_{\mathrm{A}_2}{}^{\mathrm{cis}} = 6.46 \times 10^{-9}$.[4] $k_1 = 6.7 \times 10^{-6}$ sec^{-1},[12] $k_{-1} = 1.3 \times 10^{-7}$ sec^{-1},[12] $k_3 = 2.9 \times 10^{-6}$ sec^{-1},[13] and $k_{-3} = 3.6 \times 10^{-6}$ sec^{-1},[13] with $k_2 = 4 \times 10^{-3}$ sec^{-1} and $k_{-2} = 1 \times 10^{-3}$ sec^{-1}. Because of the scatter in the present data and the different nature of the media for which the literature data are valid, no further refinement of the values of k_2 and k_{-2} was attempted. Obviously, the fit could be improved by varying the other constants also. A small change in only $K_{\mathrm{A}_1}{}^{\mathrm{tr}}$ considerably alters the best-fit values of k_2 and k_{-2} and the rather poor agreement between the value of the hydroxoaqua equilibrium constant indicated by the values given to k_2 and k_{-2} and that estimated by Bjerrum and Rasmussen[4] ($K_{\mathrm{eq}} \sim 1.5$) is not considered significant. The sum $k_2 + k_{-2} = 5 \times 10^{-3}$ sec^{-1} agrees well with the value extrapolated from data at lower temperatures by Baldwin, Chan, and Tobe.[6]

The comparison in Table I of the rate at which the cis complex loses optical activity with the calculated rate for its conversion to trans shows that isomerization alone cannot explain the rate of loss of activity. This implies that both trans and racemate cis are produced for each act of substitution leading to loss of activity.

Table I. Comparison of Rate Constants for Loss of Optical Activity (k_α) of $(-)_{589}$-*cis*-$[\mathrm{Co(en)_2(OH_2)OH}]^{2+}$ with the Calculated Values of the Rate Constant for Isomerization Cis → Trans (k_c)

pH	10^4k_α,[a] sec^{-1}	10^4k_c,[a] sec^{-1}
5.28	4.3	1.9
6.19	16.3	5.5
6.90	20.2	8.2
7.16	21.8	8.5
7.94	9.8	6.7

[a] Temperature = 25°, μ = 0.25 *M*.

Formation of $[\mathrm{Co(en)_2acac}]^{2+}$. At wavelengths near 500 nm a large and rapid change in optical density followed by a small and slow change were observed during the $[\mathrm{Co(en)_2acac}]^{2+}$ formation reaction. That is, the simplest empirical fit to the absorbance *vs.* time trace required two different exponential components. At pH's near 7 exponents in the ratio ~20:1 were estimated (*vide infra*). An obvious interpretation of these data was that consecutive rate determining reactions were occurring. However, for the reaction scheme A → B → C (where A = *cis*-$[\mathrm{Co(en)_2(OH_2)OH}]^{2+}$, C = $[\mathrm{Co(en)_2acac}]^{2+}$, and B is an unknown intermediate) the calculated values for [C] as a function of time for the two possible assignments of the measured rate constants are quite inconsistent with the amount of $\mathrm{Co(en)_2acac}^{2+}$ found after quenching the reaction mixture with acid or base and separating its components by ion exchange. For example, at a pH (~7) where the values $k_1 = 4.5 \times 10^{-2}$ sec^{-1} and $k_2 = 2.5 \times 10^{-3}$ sec^{-1} would apply, the amount of C calculated to be present at t = 300 sec would be 50% of the total Co(III), whereas the amount of $[\mathrm{Co(en)_2acac}]^{2+}$ observed was >93% of total Co (95, 93, 95% from triplicate experiments). Also, for such rate constants, a large amount of B would be present, and no evidence for such a species was found. Addition of a large excess of NaI to the unquenched reaction mixture after a similar reaction period led to rapid precipitation of $[\mathrm{Co(en)_2acac}]\mathrm{I_2 \cdot H_2O}$ in better than 70% yield. This suggests that the quenching procedures used in the precise analysis of the reaction mixture did not lead to the conversion of possible intermediates, such as $[\mathrm{Co(en)_2(OH_2)acac}]^{2+}$, to $[\mathrm{Co(en)_2acac}]^{2+}$. Further, ion-exchange separation of quenched reaction mixtures showed *trans*-$[\mathrm{Co(en)_2(OH_2)OH}]^{2+}$ as an important component, thereby demanding that reactant isomeriza-

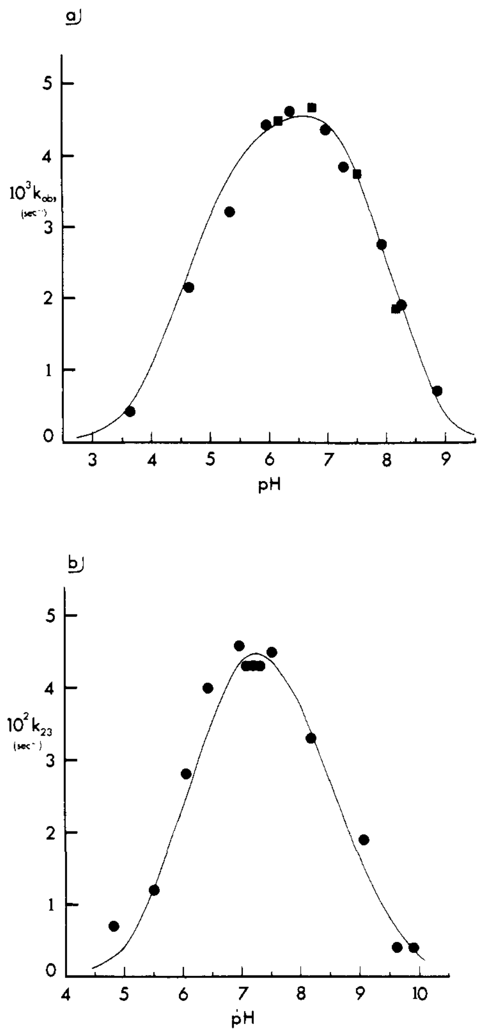

Figure 1. pH–rate profiles for processes occurring during the formation of $[\mathrm{Co(en)_2acac}]^{2+}$ from *cis*-$[\mathrm{Co(en)_2(OH_2)OH}^{2+}]$ and acetylacetone at 25° ([Co(III)] = 5 × 10^{-3} *M*, [acetylacetone] = 1.0 *M*, *I* = 1.0, NaClO$_4$): (a) reactant isomerization; (b) product formation.

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(12) Calculated from the value $k_1 + k_{-1} = 6.8 \times 10^{-6}$ sec^{-1} obtained by Kruse and Taube (ref 5) and a value of $K_{\mathrm{eq}} = k_1/k_{-1} \simeq 50$ appropriate to perchlorate media, as deduced from the data of R. C. Henney, *Inorg. Chem.*, 8, 389 (1969).

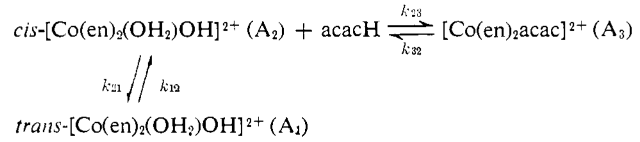
(13) M. E. Farago, B. A. Page, and C. F. V. Mason, *Inorg. Chem.*, 8, 2270 (1969).

Table II

pH	Acetyl-acetone concn (H)	$10^2\lambda_2$,[a] sec^{-1}	$10^3\lambda_3$,[a] sec^{-1}	$10^2(\lambda_2 + \lambda_3)$	$10^3(k_{12} + k_{21})$,[b] sec^{-1}	10^2k_{23}, sec^{-1}
4.79	1.00	0.77 ± 0.11	2.3 ± 0.6	1.0 ± 0.2	2.7	0.7
5.48	1.00	1.38 ± 0.09	2.5 ± 0.2	1.6 ± 0.1	3.9	1.2
6.06	1.00	2.82 ± 0.09	4.5 ± 0.3	3.3 ± 0.1	4.4	2.9
6.40	1.00	3.67 ± 0.18	7.3 ± 1.3	4.4 ± 0.2	4.5	4.0
6.97	1.00	4.67 ± 0.02	2.9 ± 0.9	5.0 ± 0.1	4.4	4.6
7.02	0.25	1.41 ± 0.08	2.3 ± 0.7	1.6 ± 0.1	4.4	1.2
7.19	0.50	2.38 ± 0.06	1.9 ± 0.3	2.6 ± 0.1	4.3	2.2
7.34	0.50	2.46 ± 0.11	2.7 ± 1.1	2.7 ± 0.2	4.0	2.3
7.13	0.75	3.31 ± 0.07	2.4 ± 0.3	3.5 ± 0.1	4.3	3.1
7.10	1.00	4.44 ± 0.11	3.0 ± 0.5	4.7 ± 0.2	4.4	4.3
7.21	1.00	4.44 ± 0.04	2.7 ± 0.7	4.7 ± 0.1	4.2	4.3
7.26	1.00	4.5 ± 0.1	1.7 ± 0.2	4.7 ± 0.1	4.2	4.3
7.44	1.00	4.3 ± 0.3	1.5 ± 0.2	4.5 ± 0.3	3.9	4.1
7.53	1.00	4.56 ± 0.06	3.21 ± 1.0	4.9 ± 0.2	3.7	4.5
7.28	1.50					6.29 ± 0.04[c]
7.07	2.00					8.8 ± 0.1[c]
7.37	2.00					9.7 ± 0.1[c]
8.20	1.00	3.0 ± 0.1	5.3 ± 4.0	3.5 ± 0.5	2.0	3.3
9.09	1.00	1.25 ± 0.23	6.3 ± 3.2	1.9 ± 0.5	0.3	1.9
9.61	1.00	0.30 ± 0.01	0.8 ± 0.6	0.4 ± 0.1	0.1	0.4
9.90	1.00	0.29 ± 0.01	1.2 ± 0.2	0.41 ± 0.03	0.1	0.4

[a] Mean of triplicate analyses. [b] Read from calculated curve fitted to isomerization data. [c] Rate constants from first-order (graphical) plots of data.

tion not be ignored in the kinetic analysis. Thus, the simplest possible reaction scheme was



$$\begin{tikzcd} cis\text{-}[Co(en)_2(OH_2)OH]^{2+}\ (A_2) + acacH \arrow[r, shift left, "k_{23}"] \arrow[d, shift right, "k_{21}"'] & {[Co(en)_2acac]^{2+}\ (A_3)} \arrow[l, shift left, "k_{32}"] \\ trans\text{-}[Co(en)_2(OH_2)OH]^{2+}\ (A_1) \arrow[u, shift right, "k_{12}"'] & \end{tikzcd}$$

High acetylacetone concentrations were used to give pseudo-first-order kinetics for the $[Co(en)_2acac]^{2+}$ formation step, and k_{32} was taken as zero, since, even at pH's well outside the range involved in this study of the formation kinetics, hydrolysis of $[Co(en)_2acac]^{2+}$ was indetectable over long periods of time. The general analytical solutions to the differential equations governing the assumed reaction scheme have been described by others[14] and for $k_{32} = 0$ become

$$A_1 = A_2^0\frac{k_{21}}{(\lambda_3 - \lambda_2)}\{e^{-\lambda_2 t} - e^{-\lambda_3 t}\}$$

$$A_2 = A_2^0\frac{1}{(\lambda_3 - \lambda_2)}\{(k_{12} - \lambda_2)e^{-\lambda_2 t} - (k_{12} - \lambda_3)e^{-\lambda_3 t}\}$$

$$A_3 = A_2^0\frac{1}{k_{12}(\lambda_3 - \lambda_2)} \times$$
$$\{(\lambda_3 - \lambda_2)k_{12} - \lambda_3(k_{12} - \lambda_2)e^{-\lambda_2 t} + \lambda_2(k_{12} - \lambda_3)e^{-\lambda_3 t}\}$$

when $A_1 = A_3 = 0$ and $A_2 = A_2^0$ at $t = 0$.

The variables λ_2 and λ_3 are algebraically complex functions of the rate constants k_{12}, k_{21}, and k_{23}.[14] However, the quantity $(\lambda_2 + \lambda_3) = k_{12} + k_{21} + k_{23}$ and since λ_2 and λ_3 are the experimental observables, the desired rate constant k_{23} is readily obtained provided k_{12} and k_{21} may be measured independently. In the present system, k_{12} and k_{21} are, of course, the $[Co(en)_2(OH_2)OH]^{2-}$ isomerization rate constants. Even when k_{12} and k_{21} are unknown, k_{23} may be estimated with good accuracy provided $k_{23} \gtrsim 5k_{12}$ (or $5k_{21}$, whichever is the greater). Then, to a good approximation

$$\lambda_2 = k_{23} + 0.5(k_{12} + k_{21})$$

$$\lambda_3 = 0.5(k_{12} + k_{21})$$

and

$$k_{23} = \lambda_2 - \lambda_3$$

At least at pH $\sim$ 7 and [acetylacetone] $\geq$ 1.0, the formation of $[Co(en)_2acac]^{2+}$ appears to be a reaction system for which this approximation is valid. As by definition,[14] $\lambda_2 > \lambda_3$ (always), there is no ambiguity (such as encountered in analysis of consecutive first-order reactions)[15] in identifying the experimental exponents with λ_2 and λ_3. The fact that near pH 7 $\lambda_2/\lambda_3 \sim 20$ then is consistent with the relationship $k_{23} > 5k_{12(21)}$. Generally, however, the values of k_{23} as a function of pH were obtained by adding λ_2 and λ_3 then subtracting the value of $(k_{12} + k_{21})$ appropriate to the given pH as read from the best fit curve to the simple isomerization rate data.

Values of λ_2 and λ_3 were initially estimated by evaluating from the final linear portion of the log $(A_t - A_\infty)$ *vs.* time plot. This was extrapolated back to zero time and λ_2 obtained from the plot of log $(A_t - A_{\text{extrap}})$ *vs.* time. Because of the small absorbance change associated with the λ_3 term, rather variable values of λ_3 were obtained by this procedure. Hence, all data were eventually analyzed by a nonlinear least-squares fitting to a function of the form[16]

$$A_t = A + Be^{-\lambda_2 t} + Ce^{-\lambda_3 t}$$

and the figures thereby obtained are summarized in Table II. Good agreement was found for the two methods of calculating λ_2 and the least-squares method gave consistent values of λ_3 from repetitive experiments

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[14] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 173–176, and references therein.

[15] N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, 66, 2110 (1970).

[16] M. R. Osborne in "Numerical Methods for Non-Linear Optimisation," F. A. Lootsma, Ed., Academic Press, 1972, p 171.

provided extensive data were used to cover later reaction times. Table II shows the dependence of the rate of $[Co(en)_2acac]^{2+}$ formation on pH and on acetylacetone concentration at the pH of maximum rate. Clearly the dependence on acetylacetone concentration is first order within experimental error. A plot of the pH dependence of k_{23} is given in Figure 1(b), the full curve being that calculated on the basis of the assumptions that both *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ and *cis*-$[Co(en)_2(OH)_2]^+$ react rapidly with neutral acetylacetone but not with the acetylacetonate anion. That is, for the reaction scheme

$$\begin{tikzcd}
cis\text{-}[Co(en)_2(OH_2)OH]^{2+} + C_5H_8O_2 \arrow[dd, shift right] \arrow[dr, "k_4"] & \\
& [Co(en)_2acac]^{2+} + 2H_2O \\
H^+ + cis\text{-}[Co(en)_2(OH)_2]^+ + C_5H_8O_2 \arrow[uu, shift right] \arrow[ur, "k_5"'] &
\end{tikzcd}$$

whence

$$k_{23} = \frac{k_4 + k_5 K_{a_2}{}^{cis}/[H^+]}{(1 + [H^+]/K_{a_1}{}^{cis} + K_{a_2}{}^{cis}/[H^+])(1 + K_a{}^{acac}/[H^+])}$$

the given curve is obtained with $k_4 = 5.0 \times 10^{-2}$ sec^{-1} and $k_5 = 3 \times 10^{-2}$ sec^{-1} when K_a(acetylacetone) = 10^{-9}.[17] The keto/enol equilibrium in acetylacetone has been ignored because under the presence experimental conditions both forms were present in large excess[18] relative to Co(III) (except perhaps for the measurements at highest pH).

The estimates of the optical purity of $[Co(en)_2acac]^{2+}$ formed from $(-)_{589}$-$[Co(en)_2(OH_2)OH]^{2+}$ at two acetylacetone concentrations were obtained from measurement of rotations at 405 nm, where $[Co(en)_2acac]^{2+}$ has a large rotatory dispersion extremum, and are given in Table III. It is apparent that paths leading to loss of optical activity in the reactant do not compete very effectively with the formation of $[Co(en)_2acac]^{2+}$. The product is stable to racemization in solution.[3]

Table III. Rotations at 405 nm for Optically Pure $(-)_{589}$-$[Co(en)_2(OH_2)OH]^{2+}$ after 2 hr Reaction at 25° with Acetylacetone Buffers, pH 7.1, $I = 1.0$ *M*, $[Co^{III}] = 5.75 \times 10^{-4}$ *M*

[acacH]	α,[a] deg	% optical purity
0.25	+0.553	91
1.0	+0.606, +0.596	94
1.0	+0.682[b]	100

[a] Path length 1 dm. [b] Solution prepared from $(-)_{589}$-$[Co(en)_2acac]I_2$ ($[\alpha]_{589} = -420°$, 0.1% in H_2O).

Most crucial in determining the mechanism of formation of $[Co(en)_2acac]^{2+}$ is the direct measurement of the degree of retention of Co–O bonds. Isolation of the $[Co(en)_2acac]^{2+}$ from ^{18}O enriched *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ as its iodide salt caused some minor complications in the present experiments, since we were able to find no convenient method of removing water of crystallization from this material. However, since the crystal water was of normal composition and provided one-third of the oxygen present in the complex, the retention of label in the $[Co(en)_2acac]^{2+}$ was simply calculated from the expression

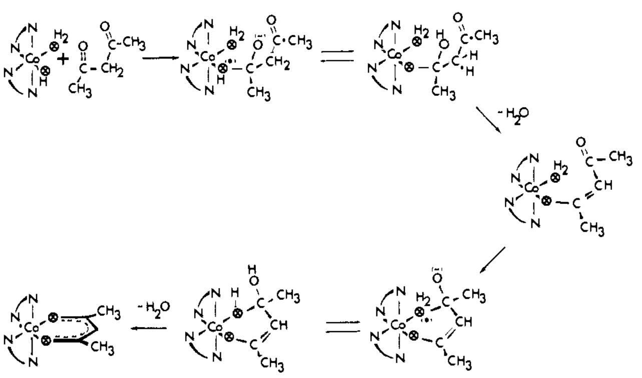

Figure 2. Proposed mechanism for the formation of $[Co(en)_2acac]^{2+}$.

$$\% \text{ retention} = 100\left\{\frac{\frac{3}{2}\left(\frac{R_{comp}}{2 + R_{comp}} - \frac{R_{CO_2}}{2 + R_{CO_2}}\right)}{\frac{R_{solv}}{2 + R_{solv}} - \frac{R_{CO_2}}{2 + R_{CO_2}}}\right\}$$

where R_{comp} is the *m/e* 46/44 ratio for CO_2 formed from $[Co(en)_2acac]I_2 \cdot H_2O$, R_{solv} is the ratio for CO_2 from the ^{18}O enriched water recovered after equilibration with *cis*-$[Co(en)_2(OH_2)_2](ClO_4)_3$ and R_{CO_2} is the ratio for normal CO_2. The results obtained are given in Table IV.

Table IV. ^{18}O Retention on Co(III) in $[Co(en)_2acac]^{2+}$ Formation

R_{CO_2}	R_{solv}	R_{comp}	% retention
0.003766	0.0968	0.0636	98
	0.1031	0.0689	102

In accord with these data the less precise results from high-resolution mass spectrometry of the thermal decomposition products of $[Co(en)_2acac]I_2 \cdot H_2O$ were *m/e* 102/100 = 0.10 ± 0.01 and *m/e* 45/43 = 0.045 ± 0.005 (from five measurements). The high mass number comes from the parent molecule ion and the low from the acetylium ion fragment with half the oxygen content of the parent species.

Discussion

The ^{18}O tracer experiment is unambiguous in demanding that both oxygen atoms in *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ be retained in the reaction with acetylacetone to form $[Co(en)_2acac]^{2+}$. Loss of label in the reactant *via* exchange with solvent is small over the reaction period. The reaction must therefore be viewed as a substitution at carbon, a facile mechanistic description being the addition–elimination processes shown in Figure 2. Within this scheme we have no indication of the relative rates of the many individual steps and it is quite possible, for example, that proton transfer

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[17] J. O. Liljenzin, *Acta Chem. Scand.*, 23, 3592 (1969), gives comprehensive and precise data on the temperature and ionic strength dependence of the gross ionization constant of acetylacetone.

[18] The ratio enol:keto for acetylacetone in aqueous solution is 0.19: see S. Forsén and M. Nilsson in "The Chemistry of the Carbonyl Group," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 203.

processes may be rate limiting. The reactive form of acetylacetone is represented as the keto tautomer since we assume that this would be more susceptible to nucleophilic attack than the enol. Certainly the inhibition of $[Co(en)_2acac]^{2+}$ formation at high pH is simply explained *if* the enolate anion is resistant to addition of Co–OH. With respect to the complex ion, the most satisfactory account of the data (Figure 1(b)) is given when both the cis hydroxoaqua and dihydroxo species are considered to undergo addition. Only the diaqua ion appears too weakly basic to form the acetylacetonate complex. The inference from this analysis is that acid catalyzed hydration of $>C{=}O$ centers arises from protonation of the carbonyl oxygen followed by attack of water and not from addition of H_3O^+.

The requirement that the reaction proceed by substitution at carbon does not necessitate that this substitution be rate determining (*vide supra*). Since many β-diketones, including, probably, acetylacetone,[19] are appreciably hydrated in aqueous solution, the possibility arises that dehydration could be rate determining in the formation of β-diketonate complexes. Consistent with such a possibility, formation rates independent of metal ion concentration have been observed for some labile metal complexes.[20] Further, the known rate of dehydration of the β-diketone acetylpyruvic acid[21] is similar to the observed rate of formation of $[Co(en)_2acac]^{2+}$. However, while the reaction scheme used to analyze the formation of $[Co(en)_2acac]^{2+}$ may be somewhat oversimplified,[22] there is no doubt that it is a sufficiently good approximation to show the first-order dependence of the formation rate on cobalt reactant concentration. This eliminates the dehydration of acetylacetone hydrate as the rate-determining step. As well, k_{23} shows a linear dependence on acetylacetone concentration up to rather high values. These facts, coupled with the analysis which gives similar rates of addition for both dihydroxo and hydroxoaqua complexes, are not inconsistent with the interpretation that k_{23} represents the rate at which the first coordinated nucleophile adds to a carbonyl center. On a general basis, it is likely that for addition processes of this kind the intermolecular step will be slower than the intramolecular, largely as a consequence of loss of translational entropy.[23] Specifically, $[(NH_3)_5CoOH]^{2+}$ attack on $H_2NCH_2COOC_2H_5$ or $H_2N(CH_2)_2COOC_2H_5$[24] is much slower than attack by the coordinated nucleophile in *cis*-$[Co(en)_2(OH)(NH_2CH_2COOC_2H_5)]^{2+}$[25] or *cis*-$[Co(en)_2(OH)(NH_2(CH_2)_2COOC_2H_5)]^{2+}$.[26] For these reasons we do not favor a mechanism in which an unfavorable preequilibrium addition is followed by a slow ring closure, even though such a mechanism might enable a more ready explanation of the apparent insensitivity of the rate of addition to basicity of the nucleophile. In any case, k_{23} must represent a lower limit to the rate of addition of CoOH to acetylacetone.

It is therefore of interest to compare this rate constant (k_{23}) with those at which other oxygen nucleophiles add to acetylacetone. Unfortunately, extensive comparisons are not possible, as the available data for oxygen exchange between acetylacetone and water[27] cover only the acid catalyzed path and in the base catalyzed cleavage of acetylacetone[19, 28] addition of OH^- to a carbonyl center is not considered to be the rate determining step. From consideration of the pH dependence of the ^{18}O exchange rates[24] an approximate upper limit of 10^{-4} sec^{-1} may be set to the rate constant ($k_{H_2O}[H_2O]$) for water catalyzed exchange. Comparison of this figure with the rate constant (k_4) for the rate of addition of *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ to acetylacetone suggests that the species CoOH adds at least 25,000 times more readily to $>C{=}O$ in acetylacetone than does HOH. Thus, it may be considered that coordination of OH^- to Co(III) generates a species predominant at neutral pH with sufficient residual nucleophilicity to yet engage in rapid substitutions at moderately activated carbonyl centers. The present estimate of the "residual nucleophilicity" of $CoOH^{2+}$ is closely similar to that estimated for the species $ZnOH^+$ when acting as a catalyst for the hydration of acetaldehyde.[29] The "trapping" of the addition product on Co(III) resolves the ambiguity encountered in labile metal systems where the general-base and nucleophilic functions of the MOH species cannot be distinguished.[29] The present data then offer support for the proposed mechanism of function of enzymes such as carbonic anhydrase[30] in which the metal ion is viewed as functioning to enhance the acidity of water by coordination, thereby generating an effective nucleophile MOH.

This study of the formation of $[Co(en)_2acac]^{2+}$ suggests an explanation of the quite disparate rates of formation of different Co(III)–β-diketonate complexes.[2] Ethyl acetopyruvate, for example, complexes with *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ at a rate at least equal to that of acetylacetone, while ethyl and methyl acetoacetate require heating for an appreciable period to achieve reaction. Acetylpyruvic acid is known to undergo very rapid addition–elimination of water,[21] while the acetoacetic acid esters would be expected to undergo such reaction less readily than acetylacetone. These ester ligands quite possibly form their bis(ethylenediamine)cobalt(III) complexes *via* normal substitution on Co. When formation is fast, however, it may be assumed that this reflects the ease of addition of nucleophiles to the β-diketone carbonyl centers. The observation that $[Co(en)_2acac]^{2+}$ formation does not proceed rapidly to completion[3] of course reflects merely the temporary diversion of some of the reactant complex to its trans isomeric form which relatively slowly rearranges back to cis and then to $[Co(en)_2acac]^{2+}$. The retention of optical activity in $Co(en)_2acac^{2+}$ formation

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(19) J.-P. Calmon and R. Maroni, *Bull. Soc. Chim. Fr.*, 3761 (1968).

(20) R. W. Taft, Jr., and E. H. Cook, *J. Amer. Chem. Soc.*, **81**, 46 (1959).

(21) J. P. Guthrie, *J. Amer. Chem. Soc.*, **94**, 7020 (1972).

(22) *E.g.*, there is no *a priori* reason to ignore a reaction path in which *trans*-$[Co(en)_2(OH_2)OH^{2+}]$ adds to acetylacetone, and this intermediate rearranges and eliminates to give $[Co(en)_2acac]^{2+}$. However, the rate of formation of $[Co(en)_2acac]^{2+}$ from *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ is relatively slow and consistent with isomerization being the rate-determining step.

(23) M. I. Page and W. P. Jencks, *Proc. Nat. Acad. Sci. U. S.*, 68, 1678 (1971).

(24) D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, unpublished results.

(25) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 92, 6151 (1970).

(26) E. Baraniak, Ph.D. Thesis, Australian National University, 1973.

(27) J. Aggett and A. L. Odell, *J. Chem. Soc. A*, 1820 (1966).

(28) R. G. Pearson and E. A. Mayerle, *J. Amer. Chem. Soc.*, **73**, 926 (1951).

(29) R. H. Prince and P. R. Woolley, *J. Chem. Soc., Dalton Trans.*, 1548 (1972).

(30) J. Coleman, *Progr. Bioorg. Chem.*, 1, 159 (1971); see also ref 26.

interrelates the absolute configurations of $(-)_{589}$-*cis*-$[Co(en)_2(OH_2)_2]^{3+}$ and $(-)_{589}$-$[Co(en)_2acac]^{2+}$ in agreement with assignments previously made on the basis of circular dichroism spectra;[31] *i.e.*, the absolute configuration is Δ.

The reactant isomerization rates not only provide data essential to the determination of the rate constant for formation of $[Co(en)_2acac]^{2+}$ but also, given an assumption of mechanism, enable some estimate to be made of reactant oxygen exchange rates. Thus, if rearrangement or substitution at Co(III) is to proceed *via* dissociation of one ligand (in the case of $Co(en)_2XY^{n+}$, dissociation of X or Y would be preferred), the oxygen exchange rates of $[Co(en)_2(OH_2)OH]^{2+}$ species must exceed the rates of isomerization and inversion. The measured rates of isomerization for *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ may therefore be regarded as lower limits to their rates of exchange and for the cis ion the lower limit may be significantly increased to the rate of its loss of optical activity. Kruse and Taube[5] have shown that for the diaqua and dihydroxo complexes the rates of exchange do not greatly exceed the rates of isomerization, and their limited data indicate that this is also probably true of the hydroxoaqua complexes. The rate of formation of $[Co(en)_2acac]^{2+}$ would then exceed the rate of oxygen exchange in *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ by an order of magnitude. From the tracer experiment it appears that such is the case.

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[31] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

Frontier Molecular Orbitals of 1,3 Dipoles and Dipolarophiles

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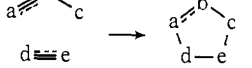
Abstract: Molecular orbital calculations have been performed by CNDO/2 and EH methods for parent and some substituted nitrilium betaines, diazonium betaines, azomethinium betaines, and carbonyl betaines and for a series of substituted alkenes. Experimental values for ionization potentials and electron affinities, calculations performed here, and calculations in the literature have been used to generate a set of frontier orbital energies and coefficients for 1,3 dipoles and dipolarophiles. The effects of substituents on orbital energies and coefficients are deduced. These frontier orbitals are of general utility in the rationalization and prediction of relative rates and regioselectivity of 1,3-dipolar cycloadditions, as well as other cycloadditions and "frontier-controlled" organic reactions.

Although fragmentary reports of the reactions of ozone, azides, and diazoalkanes with alkenes appeared prior to the 1960's,[4] the monumental work of Huisgen and coworkers led to the general concept of 1,3-dipolar cycloadditions, in which a formally zwitterionic molecule, a–b–c (the 1,3 dipole), undergoes 1,3 addition to an alkene or alkyne, d = e (the dipolarophile), to form a five-membered ring heterocycle.[5]



This reaction has been developed into a generally useful method of five-membered heterocycle synthesis, since many 1,3-dipolar species are readily available and are reactive with a wide variety of alkenes. The two all-octet resonance forms of the most common 1,3 dipoles are shown in Table I.[6]

Table I. The Common 1,3 Dipoles

Nitrilium Betaines	
$RC{\equiv}N^+C^-R_2 \leftrightarrow RC^-{=}N^+{=}CR_2$	Nitrile ylides
$RC{\equiv}N^+N^-R \leftrightarrow RC^-{=}N^+{=}NR$	Nitrile imines
$RC{\equiv}N^+O^- \leftrightarrow RC^-{=}N^+{=}O$	Nitrile oxides
Diazonium Betaines	
$N{\equiv}N^+C^-R_2 \leftrightarrow N^-{=}N^+{=}CR_2$	Diazoalkanes
$N{\equiv}N^+N^-R \leftrightarrow N^-{=}N^+{=}NR$	Azides
$N{\equiv}N^+O^- \leftrightarrow N^-{=}N^+{=}O$	Nitrous oxide
Azomethinium Betaines	
$R_2C{=}N^+(R)C^-R_2 \leftrightarrow R_2C^-N^+(R){=}CR_2$	Azomethine ylides
$R_2C{=}N^+(R)N^-R \leftrightarrow R_2C^-N^+(R){=}NR$	Azomethine imines
$R_2C{=}N^+(R)O^- \leftrightarrow R_2C^-N^+(R){=}O$	Nitrones
Oxygenated Dipoles	
$R_2C{=}O^+C^-R_2 \leftrightarrow R_2C^-O^+{=}CR_2$	Carbonyl ylides
$R_2C{=}O^+N^-R \leftrightarrow R_2C^-O^+{=}NR$	Carbonyl imines
$R_2C{=}O^+O^- \leftrightarrow R_2C^-O^+{=}O$	Carbonyl oxides
$O{=}O^+O^- \leftrightarrow O^-O^+{=}O$	Ozone

Mechanistic investigations have shown that cycloadditions of 1,3 dipoles to alkenes are stereospecifically suprafacial, solvent polarity has little effect on reaction rates, and small activation enthalpies and large negative activation entropies are generally found.[5] These facts, along with reactivity and regioselectivity phenomena, have been considered totally compatible only with a concerted four-center mechanism.[5,7] Orbital

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[3] American Chemical Society—Petroleum Research Fund Undergraduate Scholar: (a) 1971–1972; (b) 1972–1973.

[4] L. I. Smith, *Chem. Rev.*, **23**, 193 (1938).

[5] (a) R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 739; R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963); *J. Org. Chem.*, **33**, 2291 (1968); (b) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972), and earlier papers in this series.

[6] For a more complete list of 1,3 dipoles and consideration of the resonance formulation of the electronic structures of these species, see ref 5a.

[7] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 87–89.

Houk, et al. / Fronteri Molecular Orbitals of Dipoles and Dipolarophiles