in the Ni^{2+}-AEP system. A possible source of this rate retardation is indicated when the results for reaction of protonated ligand forms are discussed below.

The reaction of AEPH$^+$ with Ni(II), characterized by a k_2 of 7.3 M^{-1} sec^{-1}, is slower than that of some other diamines; for example, k_2 for nickel ions reacting with enH$^+$ is approximately 50-fold larger (where en is ethylenediamine) but is of the same order as the reactions of (N,N'-Et$_2$en)H$^+$ and phenH$^+$–8.0[4] and ~2 M^{-1} sec^{-1},[15] respectively (phen is 1,10-phenanthroline)—yet a factor of 5 less than the values of 35 M^{-1} sec^{-1} for AMPH$^+$. A "theoretical" value of k_2 for enH$^+$ of 1.7×10^3 M^{-1} sec^{-1} has been proposed,[4] and steric effects and conformational changes have been employed to rationalize reductions from the theoretical value of experimental values for enH$^+$ and protonated N-alkyl-substituted derivatives of en. Because AEP forms a six-membered ring, the theoretical value of K_o' (the outer-sphere association constant for a protonated ligand) would be somewhat higher[16] since the protonated nitrogen atom will be further away from the nickel ion when AEPH$^+$ is the ligand compared with the model amine species used, enH$^+$. Consequently in the absence of other factors k_2 would be slightly higher. This is a relatively minor determinant and the effect is in the opposite direction to the observations. Sterically controlled substitution in the case of six-membered ring chelates usually manifests itself fully in metal ions where the metal ion coordinated water bonding is more labile than in the aquonickel ion,[17] although in the case of the formation of nickel(II) β-alanine, there is some evidence of involvement of chelate ring closure in the rate-determining step. The fact that AMPH$^+$ is considerably more reactive than AEPH$^+$ toward nickel ions while the corresponding neutral ligands react with Ni^{2+} at about the same rate suggests the involvement of steric control in the reaction of AEPH$^+$ (ignoring for the moment the ICB effect for the neutral ligands).

Since the ICB effect does not operate for protonated ligands, and if we may assume that the factor $k_2(\text{AEPH}^+)/k_2(\text{AMPH}^+) \approx 1{:}5$ is entirely due to sterically controlled substitution (steric hindrance due to the proton having to be removed from the primary nitrogen for chelation, should be similar in both ligands) and that this steric factor is similar for the corresponding neutral ligands, then it may be estimated that the apparent ICB effect, which is masked in the observed rate constants, is about fivefold for AEP over AMP. However, other factors may be involved since AMP itself does not appear to be significantly activated by an ICB process in its reaction with nickel.

The energy of activation for the reaction of AEPH$^+$ with nickel(II) ions has been determined from measurements of k_f at different temperatures and pH values in the range 11-30°. The value is about 18 kcal mol^{-1} which is larger than those values which characterize reaction[2a] of uncharged ligands with nickel(II). The uncertainty in determining k_1 prevents us from obtaining a reliable value for the energy of activation in the reaction of AEP with nickel(II) although the data show that it is considerably less than 18 kcal mol^{-1}.

Registry No. Nickel, 7440-02-0; 2-(2-aminoethyl)-pyridine, 2706-56-1.

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[15] Values cited in ref 2b.

[16] In contrast to K_o. Values of K_o for interaction of nickel ions with AMP and AEP should be very similar, excluding the ICB enhancement effect.

[17] K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, 88, 4610 (1966).

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Reaction of Dimethylketene with Cobalt Carbonyl

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Recently, metal-coordinated diphenylmethylene and 1,1-diphenylvinylidene species were postulated as intermediates in decarbonylation and deoxygenation reactions of diphenylketene;[1-3] for example, Fe(CO)$_5$ reacted with diphenylketene to yield μ-(diphenylvinylidene)-bis(tetracarbonyliron)-(*Fe–Fe*).[3] We have found that dimethylketene, which is less stable than diphenylketene, is similarly deoxygenated and decarbonylated by Co$_2$(CO)$_8$. Products quite different from those reported for diphenylketene are obtained, presumably through the reaction of a dicobalt-coordinated dimethylvinylidene intermediate with a second mole of Co$_2$(CO)$_8$.

Experimental Section

Preparation of μ_3-(Isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (1) and μ_3-(Isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (2). Dimethylketene[4] (35 g, 0.50 mol) was added to a solution of Co$_2$(CO)$_8$ (55 g, 0.16 mol) dissolved in 350 ml of dry, deoxygenated hexane under nitrogen. This solution was stirred for 16 hr at 25°, and a sample of the gas above the reaction was withdrawn for mass spectral analysis. Air was bubbled through the solution for 2 hr to destroy most of the unreacted Co$_2$(CO)$_8$. The solution was then filtered, reduced to a volume of 50 ml, and chromatographed over silica gel with hexane. The dimethylketene dimer, tetramethyl-1,3-cyclobutanedione,[5] remained on the column while the substance which appeared as a purple band was eluted. The eluate was collected, and the solvent was evaporated. The residue sublimed at 50° (10^{-3} Torr), and 4.3 g [11% yield based on Co$_2$(CO)$_8$] of purple crystals was collected. The nmr and mass spectral analyses showed that this product was a 1.0:1.4 mixture of μ_3-(isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) and μ_3-(isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (2).[6] Nmr: **1** (CDCl$_3$), δ 2.37 (d, 3, J = 1 Hz), δ 5.23 (q, 1, J = 1 Hz), δ 5.43 (broad s, 1); **2** (CDCl$_3$), δ 1.49 (d, 6, J = 6.5 Hz), δ 3.75 (septet, 1, J = 6.5 Hz). Mass spectra: **1**, parent ion at m/e 482; **2**, parent ion at m/e 484. Infrared (cyclohexane): 2040 cm^{-1} (broad terminal C=O stretch). Mass spectral analysis of the gas

[1] P. Hong, K. Sonogashira, and N. Hagihara, *Nippon Kagaku Zasshi*, 89, 74 (1968). Diphenylketene is reported to react with stoichiometric amounts of Rh[(C$_6$H$_5$)$_3$P]$_3$Cl and catalytic amounts of Co$_2$(CO)$_8$ to form tetraphenylethylene. The rhodium complex is also reported to form tetraphenylallene.

[2] P. Hong, K. Sonogashira, and N. Hagihara, *Tetrahedron Lett.*, 1105 (1971). Diphenylketene is reported to react with Co$_2$(CO)$_8$ under high CO pressure to form CO$_2$ and 2-(diphenylacetoxy)-1-(diphenylmethylene)-3-phenylindene.

[3] O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 1282 (1968).

[4] Attention is drawn to the formation of sensitive, explosive peroxides if dimethylketene is contacted with air: H. Staudinger, "Die Ketene," F. Enke, Stuttgart, Germany, 1912, p 141. All operations involving monomeric dimethylketene were carried out under nitrogen.

[5] R. H. Hasek, E. U. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, 26, 700 (1961).

[6] Benzene reaction solvent gave a 1.0:0.28 ratio of **1**:**2**. Smaller scale reactions also gave an 11% yield of **1** and **2**.

collected from the reaction mixture showed the presence of CO_2, propene, and CO. The concentration of CO_2 corresponded to a molar amount approximately equal to the total amount of **1** and **2** isolated. The concentration of propene was about 2.2 times as great as that of CO_2.

One gram of the mixture of **1** and **2** was dissolved in pentane and hydrogenated with 0.5 g of 5% Pd on carbon catalyst for 2 hr at 50° and 40 psi hydrogen pressure. Pure **2** (0.73 g) was isolated and no **1** was present. *Anal.* Calcd for $C_{13}H_7Co_3O_9$, **2**: C, 32.23; H, 1.46. Found: C, 31.94; H, 1.32.[7]

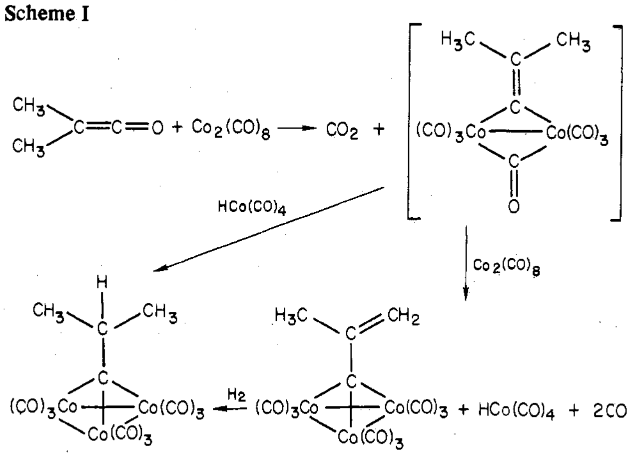
The nmr spectra were determined with a Varian Associates Model A-60D spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-110B spectrometer and a Finnigan Model 1015 S/L gas chromatograph mass spectrometer.

Results and Discussion

The reaction of dimethylketene with $Co_2(CO)_8$ under the conditions described in the Experimental Section is slower than the thermal dimerization of dimethylketene. Thus, the major product is tetramethyl-1,3-cyclobutanedione. However, significant amounts of CO_2, propene, μ_3-(isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (**1**), and μ_3-(isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (**2**) are isolated from decarbonylation and deoxygenation of dimethylketene.

We believe that the formation of **1** results from the reaction of a second mole of $Co_2(CO)_8$ with a cobalt-coordinated dimethylvinylidene intermediate. Closure of the methylidynetricobalt cluster could be accompanied by the transfer of hydride from a methyl group of the intermediate; $HCo(CO)_4$ and a carbon–carbon double bond would then result. Tetracarbonylhydrocobalt could then either liberate hydrogen, which would reduce some **1** to **2**, or add directly to the dimethylvinylidene intermediate, which would produce **2** and release 2 mol of CO. The hydrogenation of **1** to **2** was accomplished with palladium on carbon catalysts under relatively mild conditions. (See Scheme I.)

Scheme I



We believe that propene is formed in a side reaction in which $Co_2(CO)_8$ decarbonylates dimethylketene. A metal-coordinated isopropylidene intermediate is probably formed. An analogous intermediate was proposed[1] for the formation of tetraphenylethylene from diphenylketene. Propene must be released at a rate appreciably faster than the rate of dimerization to the analogous tetramethylethylene. The presence of small quantities of tetramethylethylene and 2,3-dimethylbutane in the reaction mixture was verified by gas chromatographic mass spectral analysis.

Rupilius and Orchin[8] recently proposed a mechanism whereby tetracarbonylisobutyrylcobalt may disproportionate and produce both propene and isobutyraldehyde. The possibility exists that $HCo(CO)_4$ could add directly to dimethylketene and produce tetracarbonylisobutyrylcobalt. However, gas chromatographic–mass spectral examinations of the reaction mixture, prior to the admission of air, failed to show the presence of even traces of isobutyraldehyde, butyraldehyde, isobutyric acid, or butyric acid. We therefore conclude that this is not the mechanism by which propene is formed.

An attempt to trap a dimethylvinylidene-bridged intermediate by the substitution of $Co_2(CO)_6[(C_6H_5)_3P]_2$ for $Co_2(CO)_8$ led to the quantitative formation of the reported[9] polyester **3** $[-OC[=C(CH_3)_2]C(CH_3)_2CO-]_n$. The reaction of excess dimethylketene with $Rh[(C_6H_5)_3P]_3Cl$ gave the following products: $RhCO[(C_6H_5)_3P]_3Cl$, **3**, the β-lactone dimer of dimethylketene (3-hydroxy-2,2,4-trimethyl-3-pentenoic acid, β-lactone),[10] and small amounts of both tetramethylethylene and 2,3-dimethylbutane. The polyester **3** was also obtained quantitatively from the reaction of dimethylketene with catalytic amounts of both $Fe(CO)_5$ and $Fe_2(CO)_9$.

The interesting chemistry of dimethylketene and related heterocumulenes with organometallic substrates is being investigated further.

Registry No. μ_3-(Isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*), 36974-38-6; μ_3-(isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*), 33937-52-9; $RhCO[(C_6H_5)_3P]_3Cl$, 28912-94-9.

Acknowledgment. I wish to thank Drs. Hans K. Dietl and Kent C. Brannock for their assistance through valuable discussions.

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[7] Compound **2** was reported from the reaction of $CCl_3C(CH_3)_2OH$ with $Co(CO)_4^-$: G. Palyi, F. Piacenti, M. Bianchi, and E. Benedetti, *Acta Chim. Acad. Sci. Hung.*, **66**, 127 (1970). For a recent review of $Co_3(CO)_9CY$ compounds see G. Palyi, F. Piacenti, and L. Marko, *Inorg. Chim. Acta Rev.*, **4**, 109 (1970).

[8] W. Rupilius and M. Orchin, *J. Org. Chem.*, **37**, 936 (1972).

[9] G. Natta, G. Mazzanti, G. Pregaglia, M. Binaghi, and M. Peraldo, *J. Amer. Chem. Soc.*, **82**, 4742 (1960).

[10] R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1961).

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Chemistry of Chromyl Fluoride. II.[1] A New and Useful Preparation of Chromyl Nitrate[2]

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Chromyl nitrate $[CrO_2(NO_3)_2]$ was probably first prepared by Schmiesser and Lutzow in 1954,[4] by the reaction of CrO_2Cl_2, $KClCrO_3$, or CrO_3 with N_2O_5. In our studies of CrO_2F_2 we have found a new and versatile method of preparing $CrO_2(NO_3)_2$ that does not require the preparation and handling of N_2O_5. When $NaNO_3$ is treated with excess CrO_2F_2, chromyl

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[1] Part I: W. V. Rochat, J. N. Gerlach, and G. L. Gard, *Inorg. Chem.*, 9, 998 (1970).

[2] Presented at the 27th Regional Meeting of the American Chemical Society, Corvallis, Ore.

[3] PRF Undergraduate Scholar.

[4] M. Schmiesser and D. Lutzow, *Z. Angew. Chem.*, **66**, 230 (1954).