to produce optimum agreement between the calculated and observed c_2, and hence the "best" value of k_{exch}. An example of this is given in Figure 4.

Reaction in the Gas Phase. The concentrations of species I–V are here determined by the degree of gross exchange only. If F is the fraction of *bound* CO which is $C^{18}O$ at any time, related to k_{exch} by (12), and W_r is the mole fraction of the $Ni(CO)_4$ species containing r $C^{18}O$ groups, then

$$W_r = \frac{4!}{(4 - r)!r!}F^r(1 - F)^{4-r} \qquad (16)$$

This relationship is demonstrated in Figure 5.

The rate constants were obtained as follows. The mole fraction (W_1) of $Ni(C^{16}O)_3(C^{18}O)$ was calculated for 10,000 values of F, from 0 to 1. W_1 reaches a maximum value (=0.4219) when $F = {}^1/_4$, and the maximum in the experimental absorbance–time curve (Figure 4) for a gas-phase reaction corresponds to this value. Using this relationship, for a given set of experimental data each absorbance reading was converted to mole fraction units. The value of F for each point was then obtained by interpolation from the calculated F/W_1 tabulation.

Rewriting equation 12 as follows

$$F = A\{1 - \exp(-Bk_{\text{exch}}t)\} \qquad (17)$$

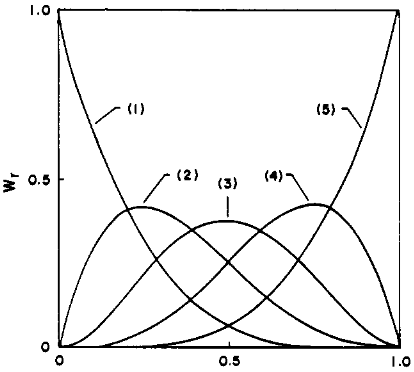

Figure 5. Relative concentrations of $Ni(C^{16}O)_n(C^{18}O)_{4-n}$ species under equilibrium conditions, calculated from eq 16. (1) $Ni(C^{16}O)_4$, (2) $Ni(C^{16}O)_3(C^{18}O)$, (3) $Ni(C^{16}O)_2(C^{18}O)_2$, (4) $Ni(C^{18}O)(C^{18}O)_3$, (5) $Ni(C^{18}O)_4$. W_r = mole fraction of the $Ni(CO)_4$ species containing r $C^{18}O$ groups. F = mole fraction of $C^{18}O$ in coordinated CO.

where A and B are known constants related to the starting conditions, then

$$\ln [1 - (F/A)] = -Bk_{\text{exch}}t \qquad (18)$$

The value of k_{exch} for each data set was determined from the slope of the linear plot of $\ln [1 - (F/A)]$ against t.

(27) G. N. Lance, "Numerical Methods for High Speed Computers," Iliffe Ltd., London, 1960, Chapter 3.

The Kinetics and Mechanism of the Thermal Decomposition of Nickel Tetracarbonyl

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Abstract: The rate of decomposition of $Ni(CO)_4$ in the gas phase has been measured, between 47.3 and 66.0°, by infrared spectrophotometry. The final stage of the decomposition occurs heterogeneously, but the preceeding steps may occur heterogeneously (<10%) or homogeneously (>90% of the total reaction under the conditions used). The homogeneous process obeys rate law 3, in which $k_{21}/k_{23} > 10^5$ l. mol^{-1} and $k_{12}k_{23}/k_{21}$ ($=k_c$, the composite rate constant) ranged from 5.67×10^{-9} to 2.80×10^{-7} mol l.$^{-1}$ sec^{-1} with activation parameters $\Delta H_c^* = 44.7 \pm 3$ kcal mol^{-1} and $\Delta S_c^* = 43 \pm 8$ eu. The most plausible mechanism is (4), and it is shown that the results are consistent with the activation parameters for CO *exchange* for which the mechanism of step 1 in (4) has been postulated. Previous studies of the thermal decomposition gave much smaller activation energies and the reasons for this discrepancy are discussed.

The rate of the decomposition of nickel carbonyl (1) in the gas phase has been extensively studied,[1–5] but some doubt still exists as to the mechanism and activation parameters of the reaction.

$$Ni(CO)_4(g) \longrightarrow Ni(s) + CO(g) \qquad (1)$$

The object of this paper is to report some new measurements of the rate of thermal decomposition and to discuss the mechanism in the light of our recent investigation[6] of the mechanism of CO exchange with $Ni(CO)_4$.

Garratt and Thompson, from a study of the photochemical and thermal decompositions,[2] postulated a mechanism (2) in which $Ni(CO)_3$ appeared as an intermediate. Assuming a steady-state concentration of

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(1) A. Mittasch, *Z. Physik. Chem.*, 40, 1 (1902).

(2) A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 524, 1817, 1822 (1934).

(3) C. E. H. Bawn, *Trans. Faraday Soc.*, 31, 440 (1935).

(4) R. K. Chan and R. McIntosh, *Can. J. Chem.*, 40, 845 (1962).

(5) A. B. Callear, *Proc. Roy. Soc.* (London), **A265**, 71 (1961).

(6) J. P. Day, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **90**, 6927 (1968).

$$\mathrm{Ni(CO)_4} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Ni(CO)_3 + CO}$$
$$\mathrm{Ni(CO)_3} \xrightarrow{k_{23}} \mathrm{Ni + 3CO} \qquad (2)$$

$\mathrm{Ni(CO)_3}$, they derived the rate law

$$\text{rate} = -\frac{d[\mathrm{Ni(CO)_4}]}{dt} = \frac{k_{12}[\mathrm{Ni(CO)_4}]}{1 + (k_{21}/k_{23})[\mathrm{CO}]} \qquad (3)$$

Experimentally, the dependence of rate on CO concentration was not studied in detail, and it was assumed that k_{12} could be obtained from the initial rate of decomposition found by extrapolation. The k_{12} so derived led to an activation energy (E_a) of 12 kcal mol^{-1}. Bawn,[3] making the same assumptions, obtained E_a = 10.2 kcal mol^{-1}; he also observed that the reaction was, in part, heterogeneous.

Chan and McIntosh,[4] in agreement with earlier work,[1] found that thermal decomposition occurred at reproducible rates only in the presence of a freshly deposited nickel surface, although most (80–90% of the reaction) occurred homogeneously in the gas phase. Using reaction vessels packed with glass wool to vary the effective surface area, they found (by pressure measurement) that the total reaction could be expressed as the sum of (a) a term independent of surface area (homogeneous reaction) and (b) a term directly proportional to surface area (heterogeneous reaction). The homogeneous reaction was found to obey a rate law of the same form as (3), and various procedures were used to derive the initial rate, and hence k_{12}. Activation parameters were calculated: $\Delta H_{12}^* = 19.1$ kcal mol^{-1} and $\Delta S_{12}^* = -16.2$ eu.

The validity of the mechanism was questioned by Callear,[5] who investigated the decomposition by flash photolysis. From the observation that the amount of decomposition was proportional to the second power of the flash energy, he concluded that two activation steps must occur in the photolysis. He proposed such a mechanism (4) for the thermal decomposition.

$$\mathrm{Ni(CO)_4} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Ni(CO)_3 + CO} \qquad \text{step 1}$$
$$\mathrm{Ni(CO)_3} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{Ni(CO)_2 + CO} \qquad \text{step 2} \quad (4)$$
$$\mathrm{Ni(CO)_2} \xrightarrow[\mathrm{Ni(s)}]{k_{34}} \mathrm{Ni(s) + 2CO} \qquad \text{step 3}$$

With the assumption that the $\mathrm{Ni(CO)_2}$ intermediate undergoes rapid decomposition, *i.e.*, $k_{34} \gg k_{32}$, this mechanism gives rise to the same rate law (3) as the previous mechanism. However, both k_{12} and k_{23} now supposedly refer to steps requiring substantial activation energy. This implies that extrapolation from experimental observations to find the initial rate, and the subsequent evaluation of k_{12}, is likely to be unreliable, since under all conditions which have so far been achieved experimentally the denominator in (3) is probably $\gg 1$.

We have recently reported[6] measurements of the rate of the nickel carbonyl substitution reaction (5), with the nucleophiles L = CO and $\mathrm{Ph_3P}$. The rates showed

$$\mathrm{Ni(CO)_4 + L} \xrightarrow{k_{\mathrm{sub}}} \mathrm{Ni(CO)_3L + CO} \qquad (5)$$

a first-order dependence on $\mathrm{Ni(CO)_4}$ concentration and were independent of the concentration or identity of the nucleophile. The rate law and the size of the activation parameters suggested a simple dissociation mechanism (6) for the process. For CO exchange in

$$\mathrm{Ni(CO)_4} \underset{\text{(slow)}}{\xrightarrow{k_{\mathrm{sub}}}} \mathrm{Ni(CO)_3 + CO}$$
$$\qquad (6)$$
$$\mathrm{Ni(CO)_3\ L} \underset{\text{(fast)}}{\longrightarrow} \mathrm{Ni(CO)_3L}$$

the gas phase, $\Delta H^* = 22.1$ kcal mol^{-1} and $\Delta S^* = 8$ eu. Also, the rate of exchange is apparently much greater than the rate of thermal decomposition at the same temperature (35°). However, according to the proposed mechanisms for thermal decomposition (2) and CO exchange (5), $k_{\mathrm{sub}} \equiv k_{12}$, and the activation parameters should be indentical.

A further point of concern is the negative entropy of activation ($\Delta S^* = -16.2$ eu) reported[4] for the thermal decomposition. A simple qualitative approach would predict a *positive* entropy change in the formation of the activated complex.

These anomalies have caused us to reinvestigate the thermal decomposition under conditions in which the dependence of rate on CO concentration could be more effectively studied than before. This was achieved by following the decomposition at much lower initial concentrations of $\mathrm{Ni(CO)_4}$ than were used previously. The $\mathrm{Ni(CO)_4}$ concentration was followed by infrared spectrophotometry, up to about 50% decomposition. Rate constants were derived from the whole decomposition process rather than by extrapolation to initial conditions. The data are consistent with a mechanism requiring two successive activation steps, and the composite activation parameters are $\Delta H_c^* = 44.7$ kcal mol^{-1} and $\Delta S_c^* = 43$ eu.

Experimental Section

General. The safety precautions necessary for the handling of nickel carbonyl, the methods of purification, storage, and analysis, and the determination of the extinction coefficient of the infrared absorption band used to follow the reaction kinetics have been discussed in the preceding paper.[6] Infrared spectrophotometry was carried out with a Perkin-Elmer 337 spectrophotometer, coupled to an external potentiometric recorder. A 1-cm path-length glass infrared cell, volume *ca.* 3 ml, with sodium chloride windows, was used (R 10-22, from International Crystal Laboratories, Irvington, N. J.).

Kinetics Measurements. The decomposition reactions were carried out, with the exclusion of light (at all times the room was illuminated by a photographic safelight; the decomposition flask was also surrounded by an opaque cloth), in a 1-l. flask fitted with a water jacket (Figure 1, flask R). The flask was connected to a vacuum line through a flexible (Tygon) connection (V), and to the infrared cell (C) through a 35-cm stainless-steel syringe needle (SN) and Teflon stopcocks (TS) (Hamilton Co., Whittier, Calif.). The reaction flask could be raised from the position shown until the syringe needle cleared the three-way stopcock (A). Experiments were carried out as follows. (1) The flask (R) was raised, evacuated (pressure 10^{-2} mm) for 20 min, filled with nitrogen (dry, $\mathrm{O_2}$ free) to 1 atm, and reevacuated. The cycle was repeated five times and the flask left under vacuum. (2) The 50-ml flask (F) was flushed out as above and the $\mathrm{Ni(CO)_4}$–CO gas mixture introduced to a measured pressure (determined experimentally to give suitable absorbance readings later). The flask was cooled in liquid nitrogen and the CO removed by repeated evacuation and flushing with nitrogen (five times). Finally, nitrogen was introduced to 1 atm and the flask was immersed in ice water. (3) The $\mathrm{Ni(CO)_4}$–$\mathrm{N_2}$ mixture was admitted to the reaction flask (R), and the pressure immediately was raised to 1 atm with nitrogen. The flask was isolated from the vacuum system and lowered into the position shown in the figure. (4) A reaction sample was admitted to the infrared cell (previously evacuated) and the absorbance measured at 2058 cm^{-1} (the absorbance maximum for the C–O asymmetric stretch). (5) The infrared cell was then reevacuated and the sampling procedure repeated at suitable intervals.

In accord with earlier observations,[4] initial experiments with a clean flask showed a variable decomposition rate. After two or three experiments, when a deposit of nickel was visible but the flask had not become opaque, faster but well-reproducible decompositions occurred for about 30 experiments. After this a sharp increase in rate often occurred with each experiment. The results we discuss later are for experiments during the intermediate "steady" period.

The extent of the simultaneous heterogeneous reaction was estimated as follows. The internal surface area of the reaction flask was *ca.* 500 cm^2. Several reactions were carried out in this flask, and then the flask was cleaned and packed with 800 cm of 2-mm diameter glass rod, cut into 3-cm lengths. This effectively doubled the surface, with insignificant (25 ml) reduction in volume. "Conditioning" of the surface was carried out as previously described. The mean rate constant for reaction in the packed vessel was from 5 to 10% greater than in the unpacked vessel at the same temperature. However, the difference is not very significant as the standard deviations are *ca.* 5%. There was no observable change in the contribution of the heterogeneous reaction over the temperature range studied. Therefore, we have not attempted to correct rates for the heterogeneous component, and the tabulated rate constants refer to data obtained from unpacked vessels.

The temperature limit for the collection of reliable data we found to be 47.3–66.0°. The thermodynamic equilibrium constant for the decomposition (Spice, *et al.*[7]) would indicate effectively complete decomposition at 47° at these concentrations (*ca.* 10^{-4} *M*). However, we observed only 60% decomposition, at equilibrium, at 47.3°, which is in reasonable agreement with the experimental observations of Mittasch.[1] Spice, *et al.*,[7] have postulated that this discrepancy is due to an increased chemical potential of a finely divided nickel surface relative to massive nickel. We did not investigate the equilibrium system further but could not obtain meaningful kinetic data below 47.3° because of the incomplete decomposition. As the temperature was raised the reaction rate increased rapidly (by a factor of 50 between 47.3 and 66.0°). The errors due to the appreciable time required for sampling the reaction mixture increased. Also, the number of readings which could be taken during the significant stage of the reaction decreased. This imposed by upper limit of 66.0° on the study of the reaction.

Calibration. The sampling procedure caused a drop in pressure in the reaction flask. Hence, repeated sampling even of a stable substance would show a decline in absorbance. To calibrate for this, stable $Ni(CO)_4$–CO mixtures were introduced into the reaction flask and successive samples withdrawn into the infrared cell. These showed a drop in absorbance per sample of 0.3%, and this factor was used to correct experimental decomposition readings. An inlet time for taking a sample between 1 and 10 sec gave identical absorbance readings, and a 3-sec sampling time was used for the kinetic measurements.

Results

We have examined the rate data in terms of the stepwise dissociation mechanism (4), which seems to us to represent the most plausible general mechanism. Making the assumption that $k_{34} \gg k_{32}$ (which is examined later), this is essentially the same mechanism as that of Garratt and Thompson (2), and gives rise to the same rate equation (3). However, the feasibility of extracting the individual rate constants, k_{12}, k_{21}, and k_{23}, depends greatly on their relative sizes and particularly on the ratio k_{21}/k_{23}. We can rewrite eq 3 thus

$$-\frac{dc}{dt} = \frac{k_{12}c}{1 + 4b(c_0 - c)} \tag{7}$$

where c = concentration of $Ni(CO)_4$ at time t, c_0 = the initial value of c, and b is the ratio

$$b = k_{21}/k_{23} \tag{8}$$

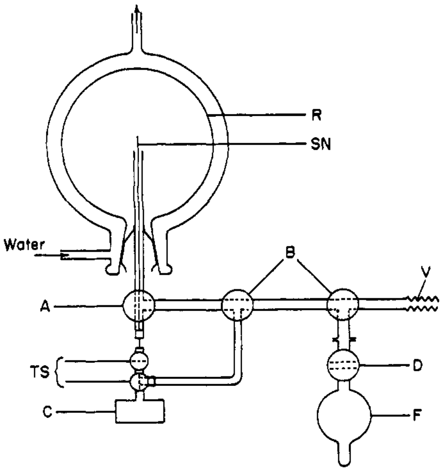

Figure 1. Apparatus for kinetic measurements: R, 1-l. flask with constant-temperature water jacket; SN, 35-cm, stainless steel syringe needle; A, B, D, glass stopcocks; TS, Teflon stopcocks; C, 1-cm infrared cell; V, flexible connection to vacuum line; F, 50-ml storage flask.

This can be integrated to give

$$[(1 + (1/4bc_0)] \ln \left(\frac{c}{c_0}\right) - \frac{c}{c_0} = -\frac{k_c t}{4c_0} - 1 \tag{9}$$

where the *composite* rate constant, k_c, is given by

$$k_c = k_{12}k_{23}/k_{21} \tag{10}$$

We can distinguish two extreme cases. If $k_{21} \ll k_{23}$, eq 7 effectively becomes a first-order equation and k_{12} could be obtained. However, if $k_{21} \gg k_{23}$, the second term in the denominator of (7) rapidly becomes the more important; this is equivalent, in eq 9, to the term $1/4bc_0$ becoming negligible compared to unity.

The data were tested initially to determine the relative sizes of k_{21} and k_{23}. The attempted first-order plot (ln c against t) was nonlinear, and it was not possible to extrapolate the curve to zero time and obtain k_{12}, as the extrapolation would be made over the region of greatest curvature. However, a good linear plot was obtained from [ln (c/c_0) − c/c_0] against t. This tests eq 9 for conditions in which $1/4bc_0$ can be ignored. Thus, from the linearity of this plot we deduced that $k_{21} \gg k_{23}$ and the slope gave an approximate value for k_c.

These preliminary treatments show that, in eq 7, b[CO] ≫ 1 under the conditions of measurement. In a typical case, the initial concentration of $Ni(CO)_4$ was *ca.* 10^{-4} *M*, and the first readings were obtained at *ca.* 3% decomposition. The CO concentration at the time of the first readings is therefore *ca.* 10^{-5} *M*, and using this estimate it can be deduced that $b > 10^5$ l. mol^{-1}.

It is now apparent that it is not feasible to obtain individually k_{12}, k_{21} and k_{23} from the rate data. However, it is possible to evaluate the composite rate constant, k_c, and to determine a lower limit for the ratio b.

For these calculations the data were treated by eq 9. The method of least squares was used to obtain the "best" straight line for a (hypothetical) plot of [(1 + $(1/4bc_0)$] ln (c/c_0) − c/c_0 against t. A value of b must be used for this plot, and this was set initially at 10^2 l. mol^{-1} and increased in steps. Between b =

(7) J. E. Spice, L. A. K. Stavely, and G. A. Harrow, *J. Chem. Soc.*, 100 (1955).

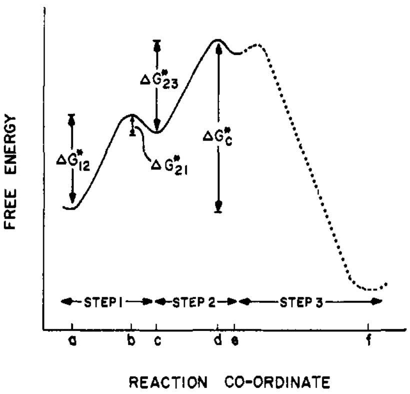

Figure 2. Energy pathway for $Ni(CO)_4$ decomposition. The solid line represents the proposed path of the homogeneous reaction; the dashed line represents an unknown, probably heterogeneous, path. Steps 1, 2, and 3 refer to the reaction mechanism 4. On the reaction coordinate, a represents $Ni(CO)_4$; b, *activated* $Ni(CO)_3$; c, $Ni(CO)_3$ intermediate; d, *activated* $Ni(CO)_2$; f, final products, Ni(s) + 4CO.

10^4 and 10^5 l. mol^{-1} an acceptable linearity was produced, the fit improving as b increased. Above $b = 10^5$ l. mol^{-1} improvement of fit became insignificant in all cases.

We carried out a final refinement by allowing a small variation in the assumed values of c_0 and the effective starting time for the reaction. Errors in these quantities can arise due to the experimental conditions. Firstly, the exact time at which the reactions "starts" is not well defined. The gas mixture, at 0°, was admitted to the reaction vessel at *ca.* 50°, and the time taken for the gas to reach this temperature could not be measured. Thus, the true zero time (t_0) may be several seconds later than the apparent zero (Bawn[3] estimated 2 sec, using pressure measurements). Secondly, the initial concentration of $Ni(CO)_4$ (*i.e.*, c_0) is known experimentally only to ±5%. We have therefore taken as the best straight line that which gave the minimum deviation from the rate data when c_0 and t_0 were treated as limited variables. The variation limits were chosen to represent the maximum experimental uncertainty; *i.e.*, c_0 was varied ±10% of the experimental value, and t_0 was varied from +10 to −10 sec. In all cases, a minimum deviation was produced within these limits, and the best value for t_0 was usually *ca.* +2 sec, which probably represents the time required for the gas to reach the temperature of the reaction vessel.

Once the behavior of the system was established, the optimum values of b, t_0, and c_0 were obtained simultaneously. The calculations were carried out on the Northwestern University CDC 6400 computer using a standard least-squares technique[8] incorporated into a program written specifically for this problem.

The optimum values of slope and c_0 give, for each data set, a value of k_c (*i.e.*, $k_{12}k_{23}/k_{21}$). Five separate experiments at the same temperature, for a fivefold variation in the starting concentration of $Ni(CO)_4$, gave a reasonably constant value of k_c with no apparent trend. The mean values of k_c at each temperature, and the standard deviations, are given in Table I. We also give 10^5 l. mol^{-1} as the *lower limit* for b.

Table I. Rate Constants and Activation Parameters[a] for the Thermal Dissociation of $Ni(CO)_4$

Temp, °C	$10^9 k_c$,[b] mol l.$^{-1}$ sec^{-1}	k_{exch},[c] sec^{-1}	k_{21}/k_{23},[d] l. mol^{-1}
47.3	5.67 ± 0.3	0.263	4.63×10^7
50.9	10.0 ± 0.5	0.354	3.54×10^7
55.0	29.8 ± 1.5	0.606	2.03×10^7
60.0	88.7 ± 4.5	1.022	1.15×10^7
66.0	280 ± 25	1.873	0.67×10^7

$\Delta H_c{}^* = 44.7 \pm 3$ kcal mol^{-1}; $\Delta S_c{}^* = 43 \pm 8$ eu

[a] Error limits are estimated, taking into account standard deviations in rate constants and general experimental uncertainties. [b] Composite rate constant for thermal decomposition. Errors indicated are standard deviations from the mean of five determinations. [c] Extrapolated first-order rate constants for CO exchange[6] in the gas phase. [d] Calculated from $k_{21}/k_{23} = k_{exch}/k_c$.

Discussion

Mechanism of Reaction. We demonstrated in the previous section that the observed rate of decomposition is consistent with the stepwise decomposition mechanism (4). The composite rate constant k_c and the derived activation parameters are given in Table I. The experimental conditions do not make it possible to determine the stepwise rate constants individually, although it is a requirement that $k_{21}/k_{23} > 10^5$ l. mol^{-1}.

We now suggest that k_{12} in the thermal decomposition can be identified with k_{exch}, the rate constant for CO exchange with $Ni(CO)_4$, mentioned earlier (5). That this is plausible is seen in Table I, column 4. Here we have calculated the quantity k_{21}/k_{23} resulting from the substitution of k_{exch} for k_{12} in k_c. The k_{21}/k_{23} so calculated is *ca.* 10^7 l. mol^{-1}, which meets the experimental requirement.

Our view of the thermal dissociation and CO exchange processes is summarized in Figure 2. The activation parameters for step 1 ($\Delta G_{12}{}^*$) are derived from the exchange experiments, and for the combined steps ($\Delta G_c{}^*$) from the decomposition experiments. The activation parameters for the second step combined with the reversal of step 1 can now be obtained.

$$\Delta H_{23}{}^* - \Delta H_{21}{}^* = \Delta H_c{}^* - \Delta H_{12}{}^* = 22.6 \text{ kcal mol}^{-1} \quad (11)$$

$$\Delta S_{23}{}^* - \Delta S_{21}{}^* = \Delta S_c{}^* - \Delta S_{12}{}^* = 35 \text{ eu} \quad (12)$$

Examining the molecular process, we suggest that the transition state in step 1 is perhaps a molecule of C_{3v} symmetry arising from a considerable elongation of one Ni–C bond in $Ni(CO)_4$. The deactivation step to the intermediate, $Ni(CO)_3$, would then be viewed as a rearrangement to, presumably, a planar molecule (D_{3h}); this arrangement reduces interatomic repulsion, and no stereochemically active nonbonded electron repulsions are anticipated. The next activation step is then viewed as the similar elongation of another Ni–C bond.

We consider first the enthalpy terms. The mean Ni–C bond dissociation energy in $Ni(CO)_4$ is 35 kcal mol^{-1} (calorimetry[9]). It is useful to consider the stepwise dissociation of the positive ions, studied by mass spectrometry.[10] The energy increases steadily

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[8] H. D. Young, "Statistical Treatment of Experimental Data," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 115.

[9] F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Am. Chem. Soc.*, 81, 800 (1959).

[10] S. M. Schildcrout, G. A. Pressley, and F. E. Stafford, *ibid.*, 89, 1617 (1967).

with successive CO removal.

$$Ni(CO)_4^+ \longrightarrow Ni(CO)_3^+ + CO \qquad 13 \pm 7 \text{ kcal mol}^{-1}$$

$$Ni(CO)_3^+ \longrightarrow Ni(CO)_2^+ + CO \qquad 39 \pm 7 \text{ kcal mol}^{-1}$$

$$Ni(CO)_2^+ \longrightarrow NiCO^+ + CO \qquad 48 \pm 7 \text{ kcal mol}^{-1}$$

$$NiCO^+ \longrightarrow Ni^+ + CO \qquad 55 \pm 7 \text{ kcal mol}^{-1}$$

It would seem reasonable to expect the same *trend* in the neutral species, *i.e.*, $\Delta H_{23}^* > \Delta H_{12}^*$, where $\Delta H_{12}^* = 22.1$ kcal mol^{-1}. If we estimate that ΔH_{21}^* is in the range 0 to +10 kcal mol^{-1}, then ΔH_{23}^* would be between 23 and 33 kcal mol^{-1}, which seems plausible.

With reference to the entropy terms, we have postulated that the molecular process for the second activation step is similar to the first, and we would therefore expect a similar entropy of activation, *i.e.*, $\Delta S_{23}^* \approx +7$ eu. On this basis, we expect $\Delta S_{21}^* \approx -28$ eu. We can test this conclusion by examining the entropy *change* for the process

$$Ni(CO)_4 \xrightarrow{\Delta S_1} Ni(CO)_3 + CO$$

for which

$$\Delta S_1 = \Delta S_{12}^* - \Delta S_{21}^* \qquad (13)$$

We make the assumption that the largest contribution to ΔS_1 comes from the liberation of one CO molecule. For CO(g), $S^\circ = 47.3$ eu, and we therefore expect ΔS_1 to be rather less than this, but negative. Then, from (13), ΔS_{21}^* should be rather less negative than -40 eu, which is consistent with our previous conclusion that $\Delta S_{21}^* \approx -28$ eu.

We conclude from the study of the entropy and enthalpy terms that, although the residual Ni–C bond energy in the transition state must be small, the outgoing CO still has greatly restricted translational freedom.

In summary, we consider that the activation parameters for CO exchange and for thermal decomposition are self-consistent, and in good agreement with the mechanism suggested for the process.

Previous Results. Our results obviously differ considerably from those of previous workers. We have concluded that only the composite rate constant (k_c) can be obtained from the rate data; previous workers derived k_{12}. Also, our value for the activation energy is more than double the previous values.

If we assume our results are correct, it can be shown that it is not possible to derive k_{12} from any of the experiments so far devised. In our experiments the starting concentration of $Ni(CO)_4$ was *ca.* 10^{-4} *M*, leading to CO concentrations at the time of initial readings, *ca.* 10^{-5} *M* (*ca.* 3% decomposition). We found that by this time, in the denominator of (3), $k_{21}[CO]/k_{23} \gg 1$. The ratio k_{21}/k_{23} has therefore a lower limit of 10^5 l. mol^{-1}. In the previous experiments, involving pressure measurements, the starting concentrations were from 10 to 50 times greater. Assuming a similar time requirement for taking measurements, at the time of the earliest measurements again $k_{21}[CO]/k_{21} \gg 1$. In these circumstances, eq 3 and 7 are indistinguishable from (14), and k_{12} cannot be

$$-\frac{dc}{dt} = \frac{k_c c}{4(c_0 - c)} \qquad (14)$$

extracted, whatever method may be used to treat the data. As we have shown, only k_c and a lower limit for k_{21}/k_{23} may be obtained.

We suggest that the previous apparent determinations of k_{12} from the decomposition experiments have been at fault in two ways, one experimental and one in the treatment of data.

Firstly, as far as can be determined from the experimental descriptions, in all previous studies the $Ni(CO)_4$ vapor was introduced into the decomposition flask from a vessel in which it had been stored for several days, possibly at room temperature. If this supposition is correct, the $Ni(CO)_4$ could have been partially decomposed before use in the kinetic experiments. This would have had an effect on the observed course of the reaction, and particularly on the initial rate, which would appear to be too slow.

In our experiments, we took precautions to remove all CO from the $Ni(CO)_4$ vapor and to store the vapor for a few minutes only, in the dark at 0°, before admitting it to the reaction vessel. In experiments in which these precautions were omitted, initial decomposition rates were indeed much slower than in normal experiments, confirming the necessity of purifying the $Ni(CO)_4$ immediately before use.

Secondly, previous workers have in various ways attempted to derive k_{12} from the *initial* rate of the reaction. In all cases the decomposition was studied by measurement of pressure, and in some cases[2,3] the initial rate was determined by measuring the slope of the (extrapolated) pressure–time curve at zero time. Chan and McIntosh,[4] who made measurements up to 10% decomposition, used three independent methods which each gave similar results. One of these used a plot derived from eq 9, which was, however, very sensitive to the value of c_0, as noted by the authors. The other two methods involved fitting the experimental data to certain general equations and making an extrapolation to zero time. However, the extrapolation is made over the region of greatest curvature (*i.e.*, the initial decomposition), and it seems to us that this treatment is inherently unreliable. Moreover, all three methods are sensitive to the zero assumed for the time scale. Although the effect of shifting this zero ±2 sec was tested (which altered the apparent initial rate by ±5%), the error could be much greater than this if predecomposition of the $Ni(CO)_4$ had indeed occurred. Chan and McIntosh also derived values of k_{21}/k_{23} ($b_2/4$ in their paper), but found them to vary considerably with initial $Ni(CO)_4$ pressure. There was no obvious reason for this at the time, but we now suggest that this supports our earlier conclusion that precise values of k_{21}/k_{23} and k_{12} cannot be extracted from this type of data.

If the rate constants are in error in this way, the effect could well be more important at the higher temperatures where the rates are greater. Thus, even if a linear Arrhenius plot was obtained, it is likely that the derived enthalpy and entropy of activation would be too small. We suggest that this could explain the differences between the previously reported activation parameters and our results.

Heterogeneous Reactions. It is apparent that there are two over-all reaction paths for the decomposition, although at the temperatures studied the heterogeneous path is probably <10% of the whole (see Experimental Section). At higher temperatures it has been concluded[11] that the heterogeneous process is more important, although in view of the large activation energy for the homogeneous process this now seems unlikely.

If we consider now the so-called "homogeneous" reaction, it is apparent that the final state or stages of this must also occur heterogeneously. Firstly, there is the experimental observation that the reaction is faster, and of more reproducible rate, when carried out in the presence of a nickel surface than in the presence of a glass surface. Secondly, the free-energy change[7] (ΔG°) for reaction 1, which refers to the formation of solid nickel, is negative only above *ca.* 80°. The hypothetical homogeneous reaction, with the formation of gaseous nickel, is only energetically favorable at much higher temperatures. Therefore, step 3 (Figure 2) must be, in part at least, heterogeneous. We assumed earlier, in order to apply eq 3, that the postulated Ni(CO)$_2$ intermediate undergoes rapid decomposition (*i.e.*, $k_{34} \gg k_{32}$). In view of the agreement between the experimental data and eq 3, and also of the magnitude of the enthalpy of activation (45 kcal mol^{-1}), which is reasonable for the removal of two CO groups, we conclude that the assumption is justified and that step 3 proceeds heterogeneously with a low enthalpy of activation.

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(11) H. E. Carlton and J. H. Oxley, *A.I.Ch.E. J.*, 13, 86 (1967).

A Proton Magnetic Resonance Study of the Stereochemistry of a Macrocyclic Schiff Base–Amine Complex of Nickel(II)

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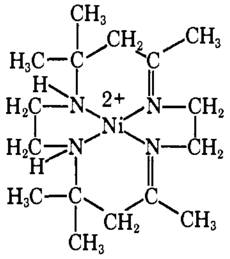
Abstract: The stereochemistry of the complex hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II) has been investigated. The data derived from proton magnetic resonance spectra and from complimentary physical chemical studies have provided detailed information concerning chelate ring conformations for three types of isomers. Differing relative positions of the two imine functions, which result in 1,4-diene and 1,7-diene forms, are readily distinguished by pmr spectra. More subtle forms of isomerism lead to *meso* and racemic forms of the 1,7-diene. These isomers have been isolated, characterized, and shown to be derived from variations in the configurations of the two asymmetric amine nitrogens. Qualitative determinations of the relative stabilities of the various ring conformations have been deduced. Homoallylic coupling through the imine bonds of the 1,7-diene isomers and a deshielding effect due to the anisotropy of the square-planer d^8 transition metal ion system have been observed.

The complex hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II), Ni(CT)$^{2+}$, first described by Curtis,[1,2] exists in a variety of isomeric forms which exhibit a number of features that are of particular stereochemical interest. Two noninterconvertible forms have been isolated by Curtis, Curtis, and Powell,[3] who have concluded on the basis of chemical and X-ray evidence that these forms are the imine positional isomers 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-dienenickel(II) (structure I, Ni(1,4-CT)$^{2+}$) and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-dienenickel(II) (structure II, Ni(1,7-CT)$^{2+}$). These were formally designated as the *cis* and *trans* isomers, respectively. The Ni(1,7-CT)$^{2+}$ isomer was also separated into interconvertible forms designated Aα and Aβ by Curtis, Curtis, and Powell, who considered them to be "conformational isomers stablized by steric hindrance."[3] We had simultaneously and independently discovered and characterized the latter isomers.[4,5]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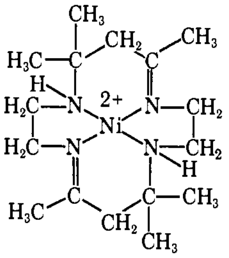
II

In the following study we discuss three types of isomerism other than imine positional isomerism that are characteristic of the Ni(CT)$^{2+}$ system. These subtle polymorphisms[4,5] are diastereoisomerism, enantiomorphism, and coordination number isomerism. Detailed attention is given to aspects of chelate ring conformations and to orientations of the peripheral methyl substituents within each of the known isomers. All structural assignments rest heavily upon interpretation of proton magnetic resonance spectra.

Results and Discussion

Coordination Number Isomerism. The coordination template condensation reaction between Ni(en)$_3$$^{2+}$

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(1) N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).

(2) N. F. Curtis and D. A. House, *Chem. Ind.* (London), 1708 (1961).

(3) N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc., A*, 1015 (1966).

(4) L. G. Warner, N. J. Rose, and D. H. Busch, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(5) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Am. Chem. Soc.*, 89, 703 (1967).