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THE MECHANISM OF THE PHOTOINDUCED HYDROGENATION OF NORBORNADIENE CATALYZED BY CHROMIUM CARBONYL COMPLEXES

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Summary

Kinetic, spectrophotometric and actinometric investigations of the hydrogenation of norbornadiene catalyzed by norbornadiene—$Cr(CO)_4$ show that the photoinduced transients promote thermal catalytic cycles.

Introduction

Our preliminary results relating to the photoinduced hydrogenation of 2,3-dimethylbutadiene, 1,3-cyclohexadiene [1], norbornadiene and 2,4-hexadiene [2] in the presence of $Cr(CO)_6$ have been previously reported. Photoinduction allows one to work at room temperature and low hydrogen pressure thus allowing higher specificity in the 1,4 reduction of conjugated dienes to monoenes. For example, photoinduced deuteration of 1,3-cyclohexadiene in the presence of $Cr(CO)_6$ yielded 100% 3,6-dideuterocyclohexene [3], while thermal deuteration in the presence of methyl benzoate—$Cr(CO)_3$ yielded cyclohexene-d_2 with 90% of the deuterium located on the α-methylene carbons and 10% on the β methylene carbons [4].

Homoconjugated norbornadiene (NB) was unusual among the dienes investigated in yielding a mixture of nortricyclene (NT) and norbornene (NN). We chose this system for our kinetic investigation of the mechanism of photoinduced hydrogenation because preliminary results have shown that a diene—$Cr(CO)_4$ complex is formed when $Cr(CO)_6$ was used as precatalyst [2] and norbornadiene—$Cr(CO)_4$ is a well-known stable compound [5] in contrast with the 1,3-diene—$Cr(CO)_4$ complexes [6, 7]. The possibility of using it as the catalyst allowed an easier investigation of changes in the catalytic species during kinetic runs.

Results

(A). Catalysis by $Cr(CO)_6$

Irradiation (λ 366 nm) of a solution of norbornadiene 6×10^{-2} *M* and $Cr(CO)_6$ 8×10^{-3} *M* in n-pentane saturated with hydrogen (partial pressure H_2 360 torr, n-pentane 400 torr at 23°), yielded a mixture of nortricyclene and norbornene in the constant ratio NT/NN = 2.80. Interestingly, this ratio is different from the thermodynamic equilibrium value at that same temperature [8]. No trace of dimer was observed under these conditions [9].

The rate of hydrogenation closely parallelled the amount of norbornadiene—$Cr(CO)_4$ formed photolytically during the first few hours (Fig. 1a and 1b). This complex thus appears to be the first catalytic entity, since hydrogenation occurs only when light is absorbed by the chromium tetracarbonyl derivative. A further 12 hours irradiation after 100% conversion caused no change of products. The absence of norbornane showed the high selectivity of the reaction.

Ultraviolet, visible and infrared spectra showed that photolysis of $Cr(CO)_6$ yielded norbornadiene—$Cr(CO)_5$ which on further irradiation was converted into norbornadiene—$CR(CO)_4$. When the norbornadiene—$Cr(CO)_5$ [ν(CO):—, 1955 s, and 1935 m cm^{-1}] is formed in a closed vessel which is then kept in the dark, the complex reacts with the carbon monoxide produced in the irradiation to give $Cr(CO)_6$ again.

The presence of several chromium complexes capable of absorbing light, the concentrations of which vary during irradiation, complicates the analysis of the kinetic runs. Since hydrogenation is dependent on the presence of the chromium tetracarbonyl complex, use of the latter as the catalyst provides an easier way of studying the mechanism of the reaction.

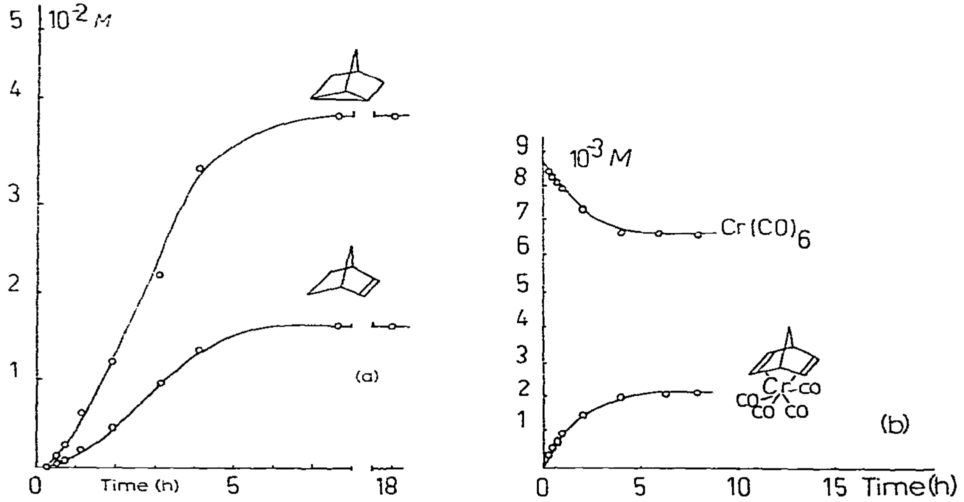

Fig. 1. Norbornadiene (5.95×10^{-2} *M*) and $Cr(CO)_6$ (8.7×10^{-3} *M*) in n-pentane. Hydrogen pressure 360 torr, λ 366 nm.

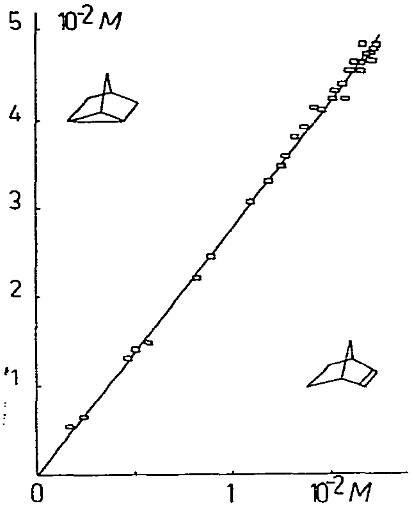

Fig. 2.

(B). Catalysis by norbornadiene—Cr(CO)$_4$

Ultraviolet, visible and infrared spectroscopy showed that the catalyst concentration remained almost* unchanged up to approximately 90% conversion of free norbornadiene. The kinetic behaviour of systems containing about 3×10^{-3} M catalyst (absorbing more than 99% of the incident light) which thus have a constant optical density is amenable to analysis.

When conversion approached 100% the solution darkened and norbornene—$Cr(CO)_5$ [ν(CO) 2070 w, 1954 s, 1945 (sh) cm^{-1}] and $Cr(CO)_6$ were formed, probably by dismutation of low coordinated or hydridochromium complexes, together with metallic Cr. The products nortricyclene and norbornene were formed in the constant ratio of 2.80 (Fig. 2), which was not dependent on the initial norbornadiene concentration. Thermal hydrogenation was not observed at 25° either before or after irradiation.

(i) Dependence on norbornadiene concentration. When the initial substrate concentration was increased from 5×10^{-3} to 5×10^{-2} M, the order of the reaction with respect to norbornadiene changed from less than first order to first order (Fig. 3). A slight deviation from first-order kinetics was however observed at the end of reaction [see section (*iii*) and Discussion].

When the substrate concentration was further increased to 3.8 M, the order varied progressively from first to zero-order (Fig. 4a and b).

A conventional rate equation [11] of form (A):

$$R = \frac{k_A \cdot [NB]}{k_B + k_C \cdot [NB]} + C \qquad \text{(A)}$$

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* The UV-visible spectrum exhibited only a very slight change during the first few minutes of irradiation, while the infrared spectrum made it obvious that a very small amount of catalyst was destroyed from the beginning of the photolysis, with concomitant formation of $Cr(CO)_6$ and traces of unidentified complexes.

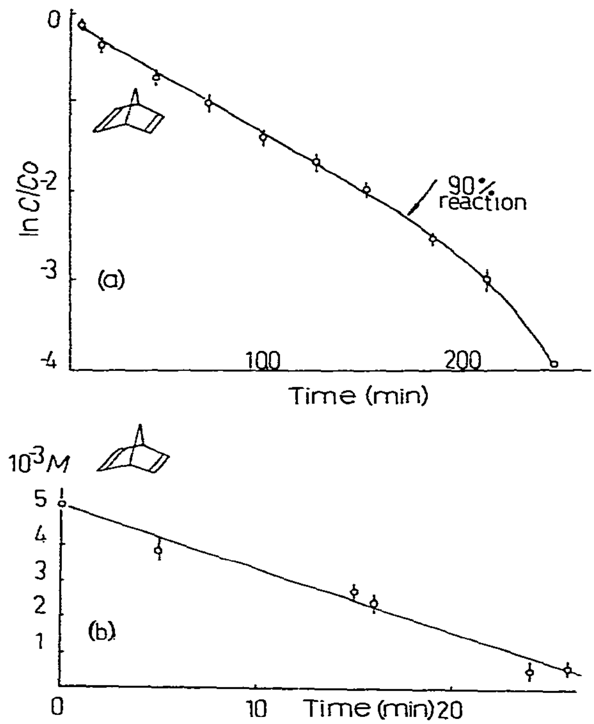

Fig. 3. NB—Cr(CO)$_4$ (3 × 10^{-3} M) in n-pentane, hydrogen pressure 360 torr, λ 366 nm; (a) [NB] 6.7 × 10^{-2} M, (b) [NB] 5 × 10^{-3} M.

does not fit the experimental results since a fifty-fold increase in the norbornadiene concentration would be necessary to observe the full transition from first to zero-order kinetics. Now, Figs. 4a and 4b show that reasonable zero-order kinetics are observed even for 4 × 10^{-1} M solutions, indicating the need for a more elaborate rate equation. Moreover, the plot given in Fig. 4c does not fit equation (A) at high norbornadiene concentrations.

(ii) Dependence on catalyst concentration. The rate varies linearly with the fraction of the incident light absorbed (Fig. 5).

$$R = \mathrm{A}\cdot I_{\mathrm{a}}\,;\, I_{\mathrm{a}} = I_0(1-e^{-\epsilon l[\mathrm{cat}]}) \qquad \text{(B)}$$

(iii) Dependence on product concentration. The rate of hydrogenation of a 7 × 10^{-2} M norbornadiene solution decreases with increasing norbornene concentrations, the order of the reaction with respect to norbornadiene decreasing from first to lower than first order (Fig. 6a). This perturbation by norbornene accounts for the slight deviation from first order kinetics found towards the end of the reaction.

The constancy of the catalyst concentration in all these runs was checked. The dependence of initial rate of reaction on initial norbornene concentration is shown in Fig. 6b. The curves are consistent with rate equation (C). Nortricyclene had no effect on the kinetics.

$$R = \frac{\mathrm{B} + k_{\mathrm{D}}\cdot[\mathrm{NN}]}{\mathrm{D} + k_{\mathrm{E}}\cdot[\mathrm{NN}]} \qquad \text{(C)}$$

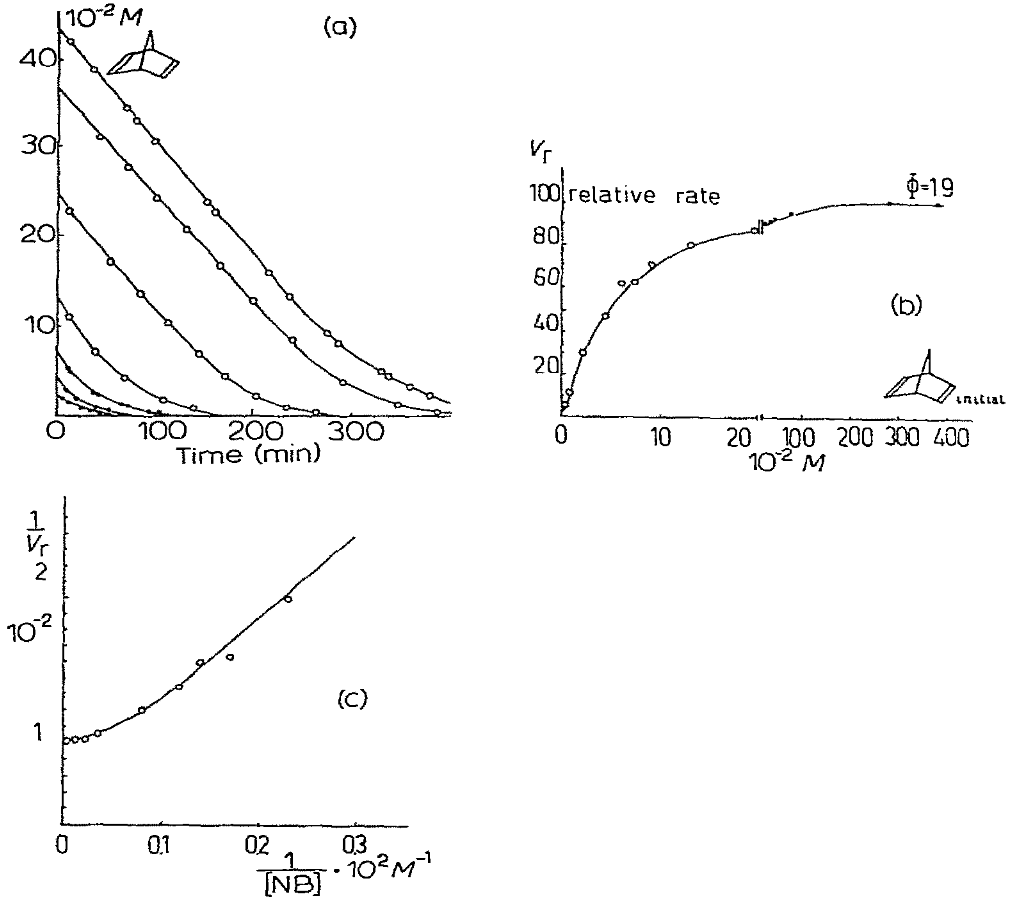

Fig. 4. NB—Cr(CO)$_4$, I_a > 99%, hydrogen pressure 360 torr, λ 366 nm.

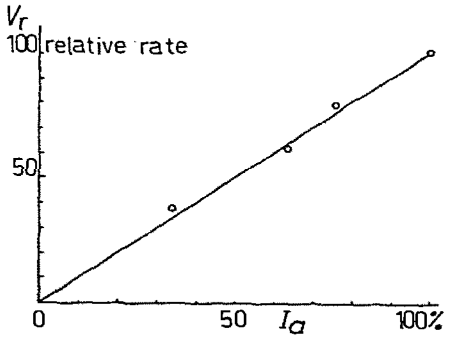

Fig. 5. NB (7.4 × 10^{-2} M), hydrogen pressure 360 torr, λ 366 nm.

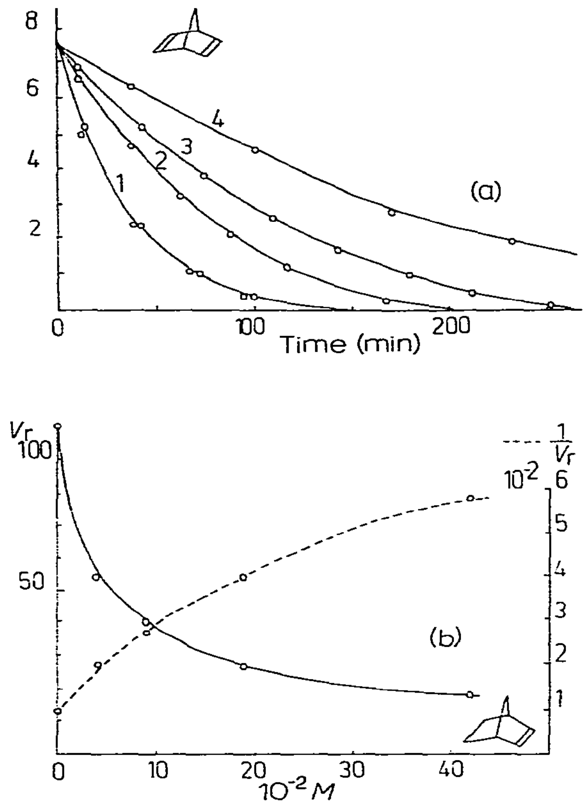

Fig. 6. The effect of changing the initial norbornene concentration: (a) 1, No NN; 2,9 × 10^{-2} M; 3, 19.6 × 10^{-2} M; 4, 4.2 × 10^{-1} M; (b) ----- is $1/V_r$, —— is V_r.

(iv) Dependence on hydrogen pressure. In order to check that the asymptotic value of the rate obtained at high norbornadiene concentrations was not caused by rate-determining dissolution of hydrogen in the solution, rate of reaction was measured as a function of the rate of stirring and the ratio of volume to surface area of the solution and were found not to change. In addition, the rate of hydrogenation is higher [7] for 1,3-cyclohexadiene than for norbornadiene under the same conditions and thus dissolution of hydrogen cannot be rate-determining with norbornadiene.

The rate of hydrogenation of norbornadiene depends on the hydrogen pressure over the pressure range 34 to 360 torr (Fig. 7). Higher pressures (i.e. total pressure > 1 atm) were not investigated.

Interestingly, a 6.5 × 10^{-2} M norbornadiene solution obeyed first-order kinetics at 360 torr H_2, but displayed lower than first-order kinetics at 156 torr H_2. The rate of hydrogenation of the catalyst in the absence of free norbornadiene also decreased with decreasing hydrogen pressure. The dependence of rate at low H_2 pressures is consistent with a rate equation of the form (D),

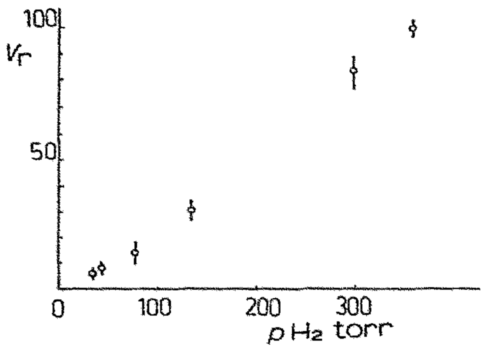

Fig. 7. [NB] = 6.5 × 10^{-2} M.

$$R = F \cdot [H_2] \qquad \text{(D)}$$

but since the reaction order was not measured at higher pressures and could possibly drop to zero, equation (E) could apply.

$$R = \frac{k_F \cdot [H_2]}{k_G + k_F \cdot [H_2]} \qquad \text{(E)}$$

(v) Quantum yield (λ 366 nm). The quantum yield for the hydrogenation of the catalyst in the absence of free norbornadiene is 0.1 ± 0.05* (hydrogen pressure 360 torr). The change in the quantum yield for the hydrogenation of norbornadiene parallels the change in initial reaction rate as plotted in Fig. 4b. The asymptotic value reached for 3.8 M norbornadiene solutions (zero-order reaction) is 1.9 ± 0.1.

(vi) Kinetic isotope effect. The rate of deuteration of a 7.5 × 10^{-2} M solution of norbornadiene in n-pentane, is the same as the rate of hydrogenation, but the ratio nortricyclene/norbornene is drastically altered (Table 1).

The products were 3,5-dideuteronortricyclene and *endo*,*endo*-5,6-dideuteronorbornene. Similar results were obtained by Cais and Rejoan [10] for the thermal deuteration of norbornadiene in the presence of arene—$Cr(CO)_3$ complexes. No scrambling of deuterium was observed and no trace of deuteronorbornadiene was detected when the reaction was stopped before completion [3].

*(vii) Solvent dependence***. Photoinduced hydrogenation of norbornadiene in the presence of norbornadiene—$Cr(CO)_4$ in dioxane is effective but the rate is lower than in aliphatic solvents. Use of a potential ligand as the solvent pro-

TABLE 1

Conditions	Irradiation time	Yield (%)	NT/NN
D_2 (360 torr)	120 min	41.7	1.8
H_2 (360 torr)	120 min	42.5	2.8

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* The quantum yield measured with higher catalyst concentrations (7 × 10^{-3} and 9 × 10^{-3} M) was 0.2 ± 0.02

** We are grateful to M. Wyart for these preliminary results.

motes the thermal destruction of the catalyst which is also decomposed by irradiation. $Cr(CO)_6$ is therefore a better precatalyst since it regenerates the tetracarbonyl complex during photolysis. The presence of 10^{-2} *M* benzene in an aliphatic solvent decreases both the rate of hydrogenation of norbornadiene and the catalyst concentration.

Discussion

(A). Primary photochemical process

We think that norbornadiene—$Cr(CO)_4$, represented by B in our kinetic schemes, yields on irradiation an open complex where one bond of the chelate is broken. This assumption is based on the following facts. Group VIB metal carbonyl complexes such as $Cr(CO)_6$ or arene—$Cr(CO)_3$ which are known to lose carbon monoxide on irradiation [12], give "low" coordinated species having a life-time of one or several seconds even in aliphatic solvents before recombination with CO or dismutation. In contrast, no long-lived intermediates could be detected when norbornadiene—$Cr(CO)_4$ was irradiated in the absence of air in a closed vessel. Moreover, thirty minutes irradiation (λ 366 nm) of 4 ml of a 10^{-3} *M* NB—$Cr(CO)_4$ solution in n-pentane swept by solvent-saturated helium (60 ml/min) resulted in no change in the concentration of the complex (visible and infrared spectroscopic analysis); the very small variation in optical density (less than 4%) can be accounted for by slight evaporation. Irradiation in the same conditions but under hydrogen pressure (360 torr) promotes as much as 10% decomposition of NB—$Cr(CO)_4$ in only 5 minutes. Evolution of carbon monoxide as the primary photolytic step may thus be discounted. We think that photoinduced incorporation of ^{13}CO would not be the right experiment to prove the eventual lability of CO ligands. Indeed, if it occurs (*a*), the quantum yield would reflect the competition between recombination and ^{13}CO incorporation and would have little significance; (*b*), eventual incorporation of ^{13}CO could possibly be the result of photoinduced opening of the diene chelate, addition of ^{13}CO followed by photoinduced chelation with release of carbon monoxide.

Wrighton, Gray and Hammond [19] proposed a model for predicting the substitutional reactivity of ligand-field excited states. Since no assignment of absorption bands has been done for norbornadiene—$Cr(CO)_4$, we do not even know what kind of excited state is reached on irradiation. The electronic absorption spectrum is given in Fig. 8. Moreover, the photochemical behaviour of olefin—metal carbonyl complexes is rather difficult to predict since both types of ligands are π-acceptors; existence of a wave-length effect in olefin—$Fe(CO)_4$ photolysis has been claimed [20].

Norbornadiene—$Cr(CO)_4$ is an interesting molecule in which photolysis seems to be limited to the chromium—diene moiety. Olefins are lower in the spectrochemical series [$W(CO)_5L$] [21], so preferential rupture of a Cr—norbornadiene bond would be favoured by the smaller ligand-field splitting. Alternatively, attack of H_2 on electronically excited norbornadiene—$Cr(CO)_4$ would only occur if the life-time of the transient was $> 5 \times 10^{-8}$ s, assuming that the diffusion rate is 10^{10} $M^{-1} \cdot s^{-1}$ and that $[H_2] \approx 2 \times 10^{-3}$ *M* under 360 torr [22].

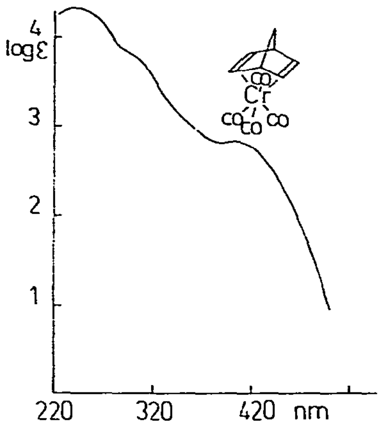


Fig. 8. Absorption spectrum of norbornadiene—Cr(CO)$_4$. ϵ_{242} 21600 ± 1%; ϵ_{300} 6400 ± 1%; ϵ_{403} 644 ± 1%.

(B). *Kinetics*

The change of reaction order with respect to the substrate is a very common feature of reactions catalyzed by transition metal complexes [11]. It is generally ascribed to a mechanism consisting of an equilibrium between the substrate and a complex containing this substrate, followed by a relatively slow reaction giving the products.

Such a reaction scheme involving a photostationary equilibrium followed by a rate-determining step is not satisfactory for the present system because it cannot account for the high quantum yield observed for the hydrogenation of norbornadiene. However, a mechanism in which the photoinduced transients promote thermal catalytic cycles, does fit the experimental data.

The results obtained in the absence of free norbornadiene are consistent with Scheme 1.

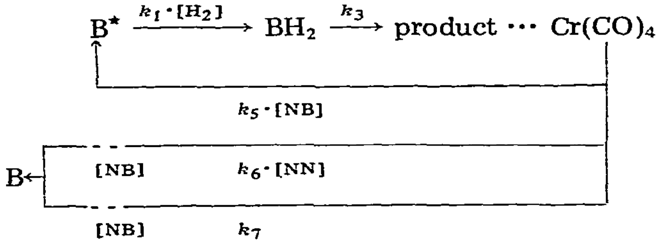
SCHEME 1

$$\begin{tikzcd}
B \arrow[r, shift left, "h\nu"] & B^{open} \arrow[l, shift left, "k_R"] \arrow[r, "k_i"] & B^{\star} \arrow[ll, bend left, "k_4"] \arrow[r, "k_1 \cdot [H_2]"] & BH_2 \arrow[r, "k_3"] & \text{product} \cdot\cdot Cr(CO)_4
\end{tikzcd}$$

The very high photostability of norbornadiene—Cr(CO)$_4$ in the absence of hydrogen and/or diene, requires that the photoinduced open complex reverts easily to B; however, it can isomerise to one of the 4 structures possible for such a pentacoordinated complex. Reaction with hydrogen yields BH$_2$, which then collapses (k_3) to yield the products bonded to Cr(CO)$_4$; NT— or NN—Cr(CO)$_4$ can only dismute in such conditions, giving NN—Cr(CO)$_5$, Cr(CO)$_6$ and probably metallic chromium. The low quantum yield (0.1) is mainly caused by the reverse reaction (k_R).

The first order kinetics observed at low norbornadiene concentrations are consistent with competitive pathways involving the substrate on one side in a rate-determining step. Since this first order behaviour coincides with a quantum yield several times higher than 0.1, it is necessary to invoke a mechanism which includes thermal catalytic cycles (Scheme 2).

SCHEME 2



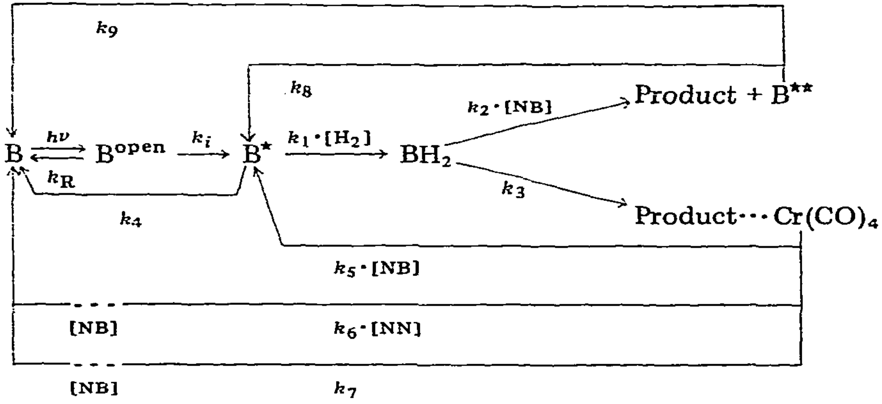
In the presence of free norbornadiene, the $Cr(CO)_4$ group bonded to the hydrogenation product will no longer dismute but will instead be scavenged (k_5) by the substrate and revert to B^*. Similarly, it may be scavenged by free norbornene (k_6), by impurities or even by the solvent (k_7). But we know that the catalyst remains almost unchanged (see Results, section B) so that any complex must revert to NB—$Cr(CO)_4$.

In the presence of increasing amounts of norbornadiene, step k_5 becomes more and more competitive and the quantum yield (the rate) increases because the small quantum yield of formation of B^* is multiplied by an increasing number of thermal cycles: $k_3 \rightarrow k_5 \rightarrow k_1 \rightarrow k_3$.

When the norbornadiene concentration is increased further, another reaction path (k_2 in Scheme 3) becomes possible, in which intramolecular H-transfer in the labile BH_2 with concomitant joining of norbornadiene to the chromium moiety occurs; a new pentacoordinated complex B^{**} is formed which can either revert to B by chelation (k_9) or to B^* (k_8). B^* can then react again with H_2 and so on. We have no experimental results concerning the structure of the labile complex BH_2. However, we know that conjugated dienes react with 1,4-addition of hydrogen [3, 7], so we assume that BH_2 is either a heptacoordinated dihydrido complex [13] with the diene in the *s-cis* conformation (norbornadiene in particular) and acting as a monodentate ligand, or possibly an octacoordinated dihydrido complex [14] with the diene acting as a bidentate ligand.

Frankel and co-workers [15] have proposed that $Cr(CO)_3$ is the active intermediate in the thermal hydrogenation of conjugated dienes in the presence of arene—$Cr(CO)_3$ complexes, while Cais and Rejoan suggest a mechanism involving successive breaking of the three bonds joining the arene moiety to $Cr(CO)_3$ [10].

SCHEME 3



The full rate equation obtained assuming steady-state concentrations for all labile chromium complexes is eqn. (F).

$$\Phi\cdot I_a = \mathrm{R} = \frac{k_1\cdot[\mathrm{H_2}]\cdot(k_2\cdot[\mathrm{NB}]+k_3)\phi_a\cdot I_a}{k_1\cdot[\mathrm{H_2}]\left[\frac{k_9}{k_8+k_9}\cdot k_2\cdot[\mathrm{NB}]+k_3\cdot\frac{k_7+k_6\cdot[\mathrm{NN}]}{k_5\cdot[\mathrm{NB}]+k_7+k_6\cdot[\mathrm{NN}]}\right]+k_4\cdot(k_2\cdot[\mathrm{NB}]+k_3)}$$

[where $\phi_a = k_i/(k_i + k_R)$] (F)

Various limiting cases may be assumed if initial rates are considered ([NN] = 0].

(1). For [NB] = 0, we obtain,

$$\mathrm{R} = \frac{k_1\cdot[\mathrm{H_2}]\cdot\Phi_a\cdot I_a}{k_4+k_1\cdot[\mathrm{H_2}]}, \qquad \text{(G)}$$

a rate equation valid for the hydrogenation of the catalyst in the absence of free norbornadiene.

(2). For [NB] sufficiently low so that $k_3 \gg k_2\cdot[\mathrm{NB}]$:

(a) If $[\mathrm{H_2}]$ is sufficiently high to allow the omission of k_4:

$$\mathrm{R} = \frac{k_5\cdot[\mathrm{NB}]\cdot\Phi_a\cdot I_a}{k_7} + \Phi_a\cdot I_a, \qquad \text{(H)}$$

a rate equation valid for [norbornadiene] $\leq 7 \times 10^{-2}$ M for $p\mathrm{H_2}$ = 360 torr.

For example, if $k_5\cdot[\mathrm{NB}] \approx 10k_7$, the reaction will appear to be first order and the quantum yield will be $11\Phi_a\cdot I_a$ i.e., 1.1 [see Results, section B (*v*)].

(b) If $k_1\cdot[\mathrm{H_2}] \ll k_4$:

$$\mathrm{R} = \frac{k_1\cdot[\mathrm{H_2}]\cdot\Phi_a\cdot I_a}{k_4}, \qquad \text{(I)}$$

i.e., when the hydrogen pressure is drastically decreased, then the reaction order with respect to norbornadiene drops to zero and the rate is linearly dependent on $[\mathrm{H_2}]$.

(3). For [NB] sufficiently high so that $k_2\cdot[\mathrm{NB}] \gg k_3$, then we obtain:

$$\mathrm{R} = \frac{k_1\cdot[\mathrm{H_2}]\cdot\Phi_a I_a}{k_1\cdot[\mathrm{H_2}]\cdot k_9/(k_8+k_9)+k_4}, \qquad \text{(J)}$$

an equation giving zero order kinetics when [norbornadiene] > 1*M*.

The pseudo-zero order kinetics observed with lower norbornadiene concentrations arise from the full rate equation (F) involving both reaction paths k_3 and $k_2\cdot[\mathrm{NB}]$.

(4). When [NB] is sufficiently low for $k_3 \gg k_2\cdot[\mathrm{NB}]$ and [NN] is high enough for $k_6\cdot[\mathrm{NN}] \gg k_7$, eqn. (K) applies.

$$\mathrm{R} = \frac{k_1\cdot[\mathrm{H_2}]\cdot\Phi_a\cdot I_a\cdot(k_5\cdot[\mathrm{NB}]+k_6\cdot[\mathrm{NN}])}{k_4\cdot k_5\cdot[\mathrm{NB}]+(k_1\cdot[\mathrm{H_2}]+k_4)\cdot k_6\cdot[\mathrm{NN}]} \qquad \text{(K)}$$

Comparison of the set of equations (B)—(E) with the set (F)—(K) supports the mechanism proposed.

The absence of a kinetic isotope effect agrees well with the scheme since these experiments were performed under conditions corresponding to equation

(H) when the rate is only dependent on the competition between $k_5 \cdot [NB]$ and k_7. Nevertheless, the relative heights of the potential energy barriers characterizing k_3 and leading either to nortricyclene or to norbornene seems to be isotope-dependent.

The absence of any scrambling in the products or incorporation of deuterium into the dienes leads to the conclusion that k_3 and k_2 are irreversible steps. Irreversibility of the addition step has also been postulated for the thermal deuteration of conjugated fatty esters in the presence of methyl benzoate—$Cr(CO)_3$ [4]. Although thermal catalytic cycles are involved in the mechanism, the amount of diene converted after interruption of the irradiation is negligible.

Experimental

Norbornadiene (U.C.B.) was purified by preparative VPC on an n-butyl tetrachlorophthalate column. $Cr(CO)_6$ (Strem Chemicals Inc.) and norbornadiene—$Cr(CO)_4$ [16] were sublimed before use. n-Pentane P.A. (U.C.B.), hydrogen (Oxhydrique Int. qual. A) and deuterium (Matheson) were used without further purification.

All solutions were deaerated by several freezing, pumping and thawing cycles (10^{-4} torr) before saturation with hydrogen. The solutions were thoroughly stirred during irradiation and the free volume of gaseous hydrogen was such that consumption could be neglected.

All irradiations were performed with an HPK 125 watt lamp fitted with a Kodak filter (λ 366 nm).

Analyses (norbornadiene, nortricyclene and norbornene) were performed by VPC on an n-butyl tetrachlorophthalate column (2.5 m). The absence of norbornane was checked using an ethylene glycol column.

The quantum yields were measured using potassium ferrioxalate as an actinometer [17] and the results were checked by measuring the quantum yield for the photoreduction of acridine in methanol [18] on the same optical bench.

Infrared spectra were obtained with a Perkin—Elmer 356 instrument using a 0.5 mm pathlength NaCl cell sealed to the reaction cell and fitted with a degassing stop-cock. A Unicam SP 1800 was used for ultraviolet and visible analyses.

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