

PHOTOCATALYTIC HYDROGENATION OF DIENES WITH CHROMIUM CARBONYLS

MANFRED J. MIRBACH *, TUYET NHU PHU and ALFONS SAUS

Universität Duisburg, Gesamthochschule, Lotharstrasse 63, 4100 Duisburg (West Germany)

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Summary

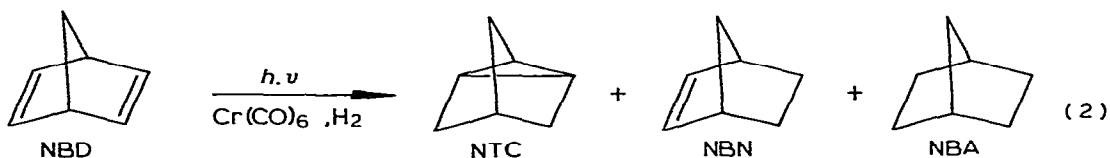
The photochemical hydrogenation of norbornadiene (NBD) in the presence of $\text{Cr}(\text{CO})_6$ or $\text{Cr}(\text{CO})_4\text{NBD}$ at normal pressure yields nortricyclene (NTC) and norbornene (NBN) in a ratio of 3/1. With increasing hydrogen pressure the NTC/NBN ratio changes to 0.8/1 at 100 bar H_2 , due to a faster formation of norbornene. The formation of NBN is more strongly inhibited than that of NTC by 50 bar of CO. Other conjugated dienes such as cyclohexadiene, isoprene, or 1,3-pentadiene give exclusively 1,4-hydrogenation products. The results are rationalized by a mechanism in which the 1,4-addition and the NTC formation are initiated by a CO dissociation, whereas the norbornene is formed via initial cleavage of a Cr–diene bond in the $\text{Cr}(\text{CO})_4$ diene catalyst.

Introduction

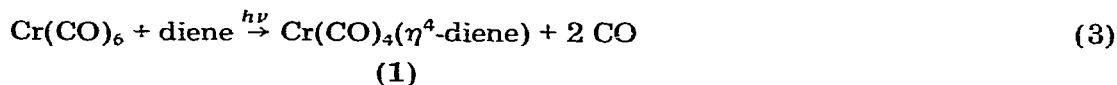
The photochemical hydrogenation of conjugated dienes with chromium carbonyl catalysts is one of the more important examples of use of UV light in homogeneous catalysis [1,2]. The reaction leads specifically to 1,4-addition in the case of conjugated dienes, giving *cis* monoenes (eq. 1) [2–4].



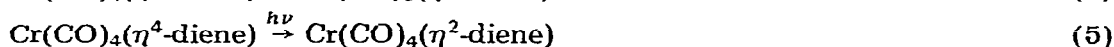
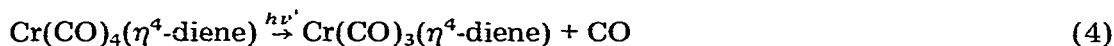
With norbornadiene (NBD) as the substrate three products are obtained, namely nortricyclene (NTC), norbornene (NBN), and norbornane (NBA) (eq. 2) [5–7].



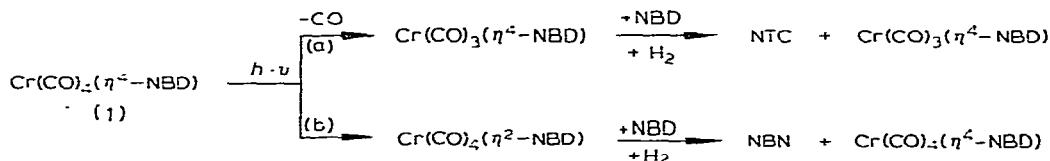
Several mechanistic studies have been performed on this reaction. All the investigators agree that the first step is the reaction of chromium hexacarbonyl with the diene to form a $\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$ complex (eq. 3).



The subsequent processes are still controversial. Two main possibilities are usually considered. The first is based on the idea that photochemical excitation of the chromium carbonyl diene complex 1 leads to extrusion of carbon monoxide (eq. 4) [11,12]. The second involves cleavage of the chromium—olefin bond as the primary photochemical reaction of complex 1 (eq. 5) [8–10].



It has been suggested that in the case of norbornadiene both mechanisms are operative, and that nortricyclene is formed via CO dissociation and norbornene via Cr—olefin bond cleavage (Scheme 1) [14].



SCHEME 1

Alternative (b) has also been thought to be responsible for the thermal hydrogenation of dienes catalyzed by complex 1 at temperatures $>50^\circ\text{C}$ and for thermal substitution reactions of 1 with other ligands [13–16].

There remain, however, a number of questions which must be answered in order to account satisfactorily for the details of the photochemical hydrogenation of dienes:

(a) Why do conjugated dienes undergo exclusively 1.4-addition, whereas norbornadiene undergoes 1.3-, 1.2- and total hydrogenation?

(b) What is the exact catalytic cycle and why does the reaction not proceed thermally to completion, since in the absence of free CO the repeating unit $\text{Cr}(\text{CO})_3(\eta^4\text{-NBD})$ has no obvious way of re-forming the starting complex 1.

(c) Assuming that the hypothesis of the Cr—olefin bond cleavage initiating the hydrogenation is correct, how can a η^2 -coordinated diene add H_2 in 1.4 positions?

Since the answer to these and similar questions should contribute to a better understanding not only of the chromium carbonyl catalyzed hydrogenation of dienes, but also to photocatalytic reactions with transition metal carbonyls in general, we have carried out studies of the influence of H_2 and CO pressure on the photochemical hydrogenation of norbornadiene and other conjugated dienes. (For a preliminary report see reference [7].)

Results

When a diene and $\text{Cr}(\text{CO})_6$ are irradiated under hydrogenation conditions the solution immediately turns yellow due to the formation of the $\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$ complex, which is the actual catalyst for the hydrogenation. The complex can be readily isolated when norbornadiene is used as the diene, but such isolation is more difficult for conjugated dienes [4,12].

As catalysts for the hydrogenation of NBD $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_4(\eta^4\text{-NBD})$ give similar results (Table 1), but with $\text{Cr}(\text{CO})_6$ an induction period and a lower reaction rate are observed due to the initial formation of $\text{Cr}(\text{CO})_4(\eta^4\text{-NBD})$ (eq. 3). Additionally a striking effect of H_2 pressure is observed: the first order increase of the reaction rate with H_2 pressure is exclusively due to the faster formation of norbornene, the nortricyclene yield being nearly independent of pressure. This causes the NTC/NBN ratio to drop from $\sim 3/1$ at normal pressure to 0.8/1 at 100 bar H_2 . (See Fig. 1 and 2.) At higher pressures small but significant amounts of norbornane are formed. Careful analysis of the rates at various pressures reveals, that the increase in the NBA yield is accompanied by an identical decrease in the NTC yield (Table 1). Since neither free NBN nor free NTC are hydrogenated under these conditions, the NBA must be formed by hydrogenolysis of a complex in which NTC is still coordinated to the chromium.

The reaction rate is first order with respect to the NBD concentration, even at high H_2 pressure. The photochemical quantum yield for the hydrogenation at 90 bar H_2 pressure and a NBD-concentration of 0.15 M is $\phi(280 \text{ nm}) = 0.32$; $\phi(366 \text{ nm}) = 0.25$.

TABLE 1

INFLUENCE OF HYDROGEN PRESSURE ON THE PHOTOCHEMICAL HYDROGENATION OF NORBORNADIENE. 0.15 M norbornadiene in 1 ml n-decane, 3.4×10^{-3} M catalyst, 15 min irradiation with a 1000 W Hg-Xe lamp through Pyrex. T 20°C. NBD = norbornadiene, NTC = nortricyclene, NBN = norbornene, NBA = norbornane

$P(\text{H}_2)$ (bar)	Concentration (mmol. l ⁻¹)				NTC/NBN ratio	Yield (%) NTC + NBA
	NBD	NBN	NTC	NBA		
With $\text{Cr}(\text{NBD})(\text{CO})_4$						
1	80	17	51	0.3	3.0	34
10	75	27	51	0.7	1.9	34
30	68	36	45	2.4	1.3	32
40	68	39	44	3.8	1.1	32
70	49	47	42	8.4	0.9	34
100	42	51	44	10.8	0.9	36
With $\text{Cr}(\text{CO})_6$						
1	124	6	19	0	3.2	13
5	105	9	25	0	2.8	16
20	113	13	23	0.4	1.8	15
30	107	15	25	0.4	1.7	17
40	111	16	22	0.6	1.4	15
70	198	20	24	0.9	1.2	17
100	104	22	22	1.2	1.0	16

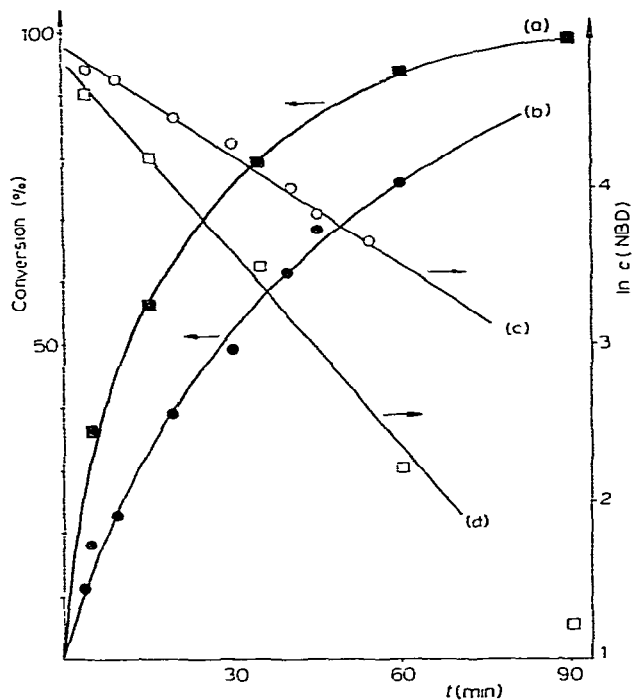


Fig. 1. Photochemical hydrogenation of norbornadiene (NBD): (a) NBD conversion (%) with $\text{Cr}(\text{NBD})(\text{CO})_4$ as catalyst (left ordinate); (b) NBD conversion (%) with $\text{Cr}(\text{CO})_6$ as catalyst (left ordinate); (c) \ln NBD concentration with $\text{Cr}(\text{CO})_6$ as catalyst (right ordinate); (d) \ln NBD concentration with $\text{Cr}(\text{NBD})(\text{CO})_4$ as catalyst. Conditions: NBD concentration 0.15 M in *n*-decane (1 ml), $P(\text{H}_2)$ 30 bar for $\text{Cr}(\text{NBD})(\text{CO})_4$ -experim. and 80 bar for $\text{Cr}(\text{CO})_6$, T 20°C, 1000 W Hg/Xe-lamp/Pyrex.

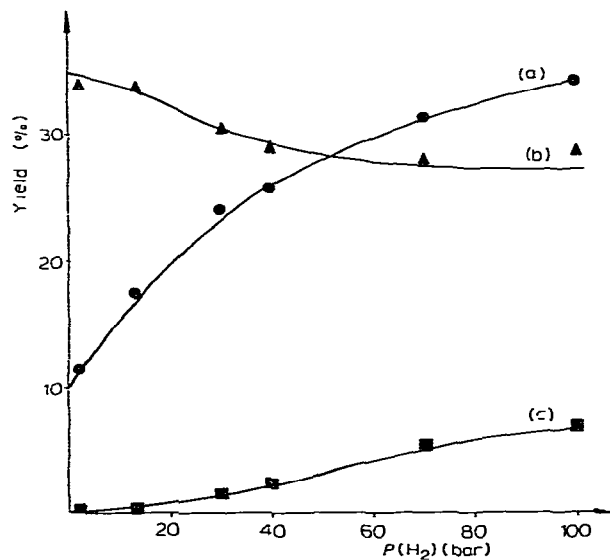


Fig. 2. Pressure dependence of the $\text{Cr}(\text{NBD})(\text{CO})_4$ photocatalyzed hydrogenation of norbornadiene: (a) norbornene yield; (b) nortricyclene yield; (c) norbornane yield. Conditions: see Table 1.

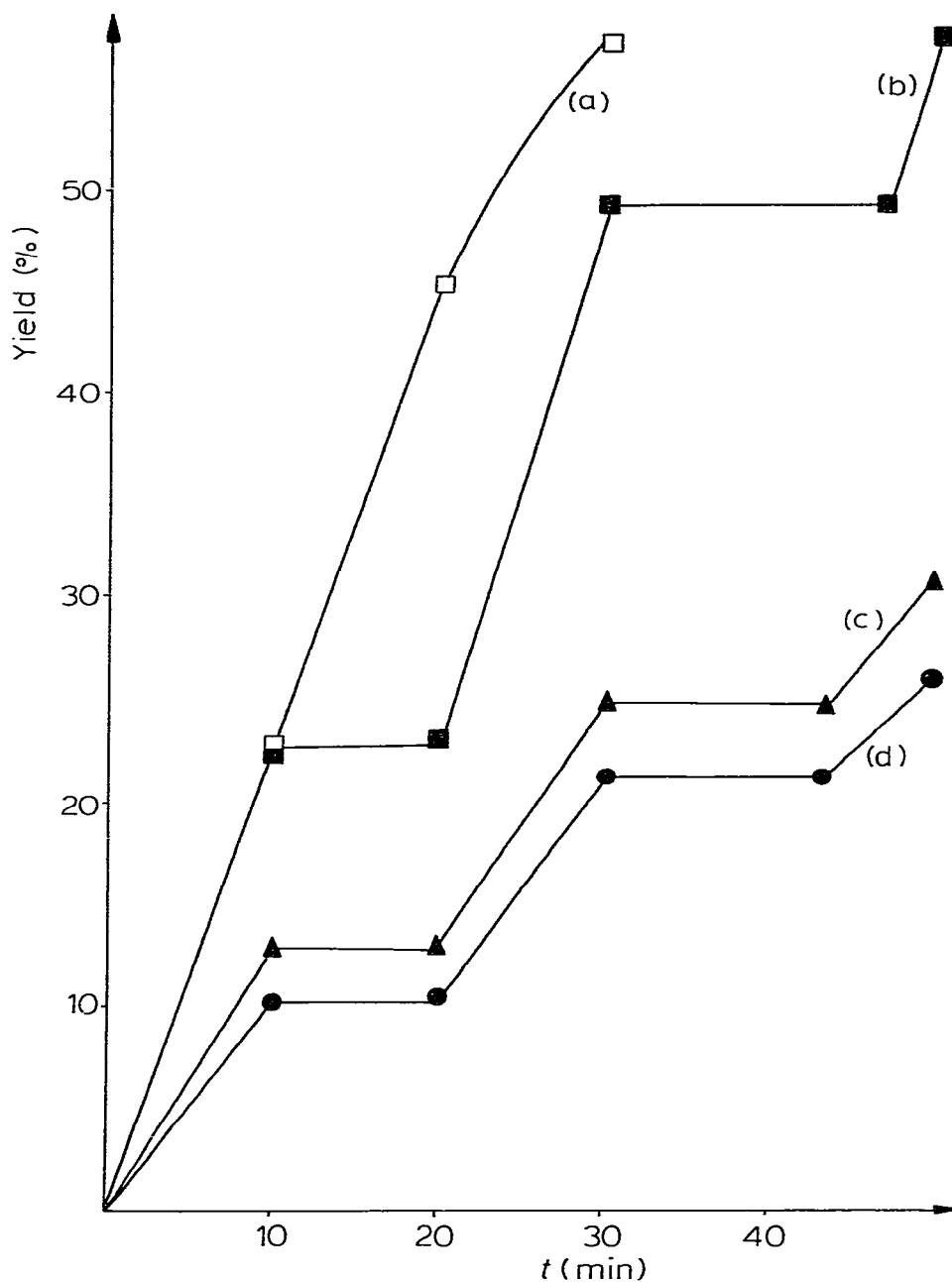


Fig. 3. Photochemical hydrogenation of norbornadiene with alternating irradiation and dark periods. (a) NBD conversion with continuous irradiation; (b) NBD conversion with intermitting irradiation; (c) NTC yield; (d) NBN yield. $P(\text{H}_2)$ 100 bar. Conditions: see Table I.

The quantum yield is independent of the light intensity or, in other words, the rate increases linearly with increasing light intensity. Since the quantum yield of the stoichiometric hydrogenation of $\text{Cr}(\text{CO})_4\text{NBD}$, in the absence of free NBD, is reported to be $\phi = 0.1$, only 2 to 3 thermal cycles follow one photo-

chemical step under the catalytic conditions used in our experiments. Thereafter a new photon is needed to continue the hydrogenation. This is also reflected in an experiment with intermittent irradiation (Fig. 3): Products are only formed when the light is on and the hydrogenation of NBD ceases immediately when the light is turned off.

Effect of carbon monoxide

At a hydrogen pressure of 50 bar the hydrogenation of norbornadiene proceeds fairly rapidly and a conversion of ~50% is reached after 30 min of irradiation. The NTC/NBN product ratio under these conditions is ca. 1. When an increasing partial pressure of carbon monoxide is added the rate decreases considerably, and the NTC/NBN ratio approaches 2 at 50 bar CO and 50 bar H₂ (Table 2). A decrease in the H₂ partial pressure at 50 bar CO leads to a lower conversion rate, without changing the product ratio very much. In the presence of carbon monoxide the reaction rate decreases at higher temperatures, but the product distribution remains approximately constant (Table 2).

During the hydrogenation the starting catalyst reacts with the added CO to form Cr(CO)₆ (Fig. 4). It should be noted, however, that the effect of CO is not as large as one might suspect. At a CO partial pressure of 10 bar a considerable amount of the Cr(CO)₄NBD survives 30 min of irradiation and the formation of hydrogenated products is only moderately suppressed.

Conjugated dienes

Conjugated dienes react in the presence of Cr(CO)₆ and H₂ to give exclusively 1.4-hydrogenated products even at high H₂ pressure and the activities (and quantum yields) increase in the order 1.3-pentadiene < isoprene < 1.3 cyclohexadiene.

The product cyclohexene could, of course, be formed via 1.2- or 1.4-hydrogenation, but deuteration experiments have shown that the 1.4-position of 1.3-cyclohexadiene is actually attacked [5].

TABLE 2

INFLUENCE OF CARBON MONOXIDE ON THE PHOTOCHEMICAL HYDROGENATION OF NORBORNADIENE. 0.15 M norbornadiene, 3.2×10^{-3} M Cr(NBD)(CO)₄ in 1 ml n-decane, P(H₂) 50 bar; 1000 W Xe-Hg-lamp, pyrex filter. (NBN = norbornene, NTC = nortricyclene, NBA = norbornane)

T (°C)	Reaction time (h)	P(CO) (bar)	Yield (%)			% of total hydrogenation products			Conversion (%)
			NBN	NTC	NBA	NBN	NTC	NBA	
20	0.5	0	24.5	25.1	2.1	47.4	48.5	4.1	62
20	0.5	10	9.1	11.6	0.2	43.5	55.5	1.0	25
20	0.5	22	4.1	6.6	0	38.3	61.7	0	12
20	0.5	30	1.9	3.2	0	37.3	62.7	0	10
20	0.5	50	1.5	2.7	0	35.7	64.3	0	7
20	0.5	50 ^a	1.2	2.0	0	36.8	63.2	0	4
60	15	10	17.4	28.7	4.7	34.3	56.5	9.2	55
90	15	10	10.6	18.6	1.2	34.8	61.2	4.0	31

^a P(H₂) 20 bar.

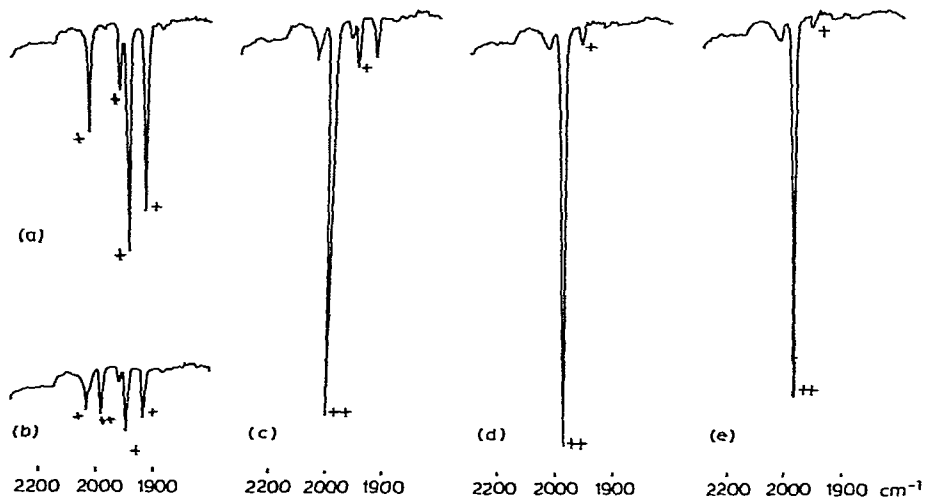


Fig. 4. IR spectra of the catalyst in the CO stretching region after the hydrogenation of norbornadiene in the presence of carbon monoxide. (Reaction conditions as in Table 2): (a) Starting solution; (b) 50 bar H_2 , 0 bar CO, 30 min, $20^\circ C$; (c) 50 bar H_2 , 10 bar CO, 30 min, $20^\circ C$; (d) 50 bar H_2 , 22 bar CO, 30 min, $20^\circ C$; (e) 50 bar H_2 , 10 bar CO, 15 h, $90^\circ C$; + absorption bands of $Cr(CO)_4(\eta^4-NBD)$; ++ absorption bands of $Cr(CO)_6$.

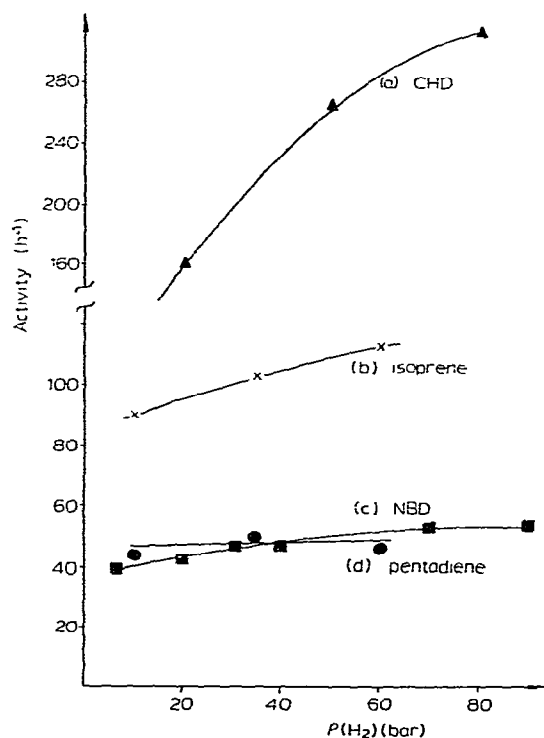


Fig. 5. Catalytic activity of $Cr(CO)_6$ for the photochemical hydrogenation of dienes at various hydrogen pressures: (a) 0.07 M 1,3-cyclohexadiene, 0.0011 M $Cr(CO)_6$ in 1 ml n-decane, t 3 min; (b) 0.25 M isoprene, 0.0038 M $Cr(CO)_6$ in 1 ml n-decane, t 30 min; (c) 0.15 M norbornadiene, 0.0034 M $Cr(CO)_6$ in 1 ml n-decane, t 15 min; (d) 0.25 M 1,3-pentadiene, 0.0049 M $Cr(CO)_6$ in 1 ml n-decane, t 15 min.

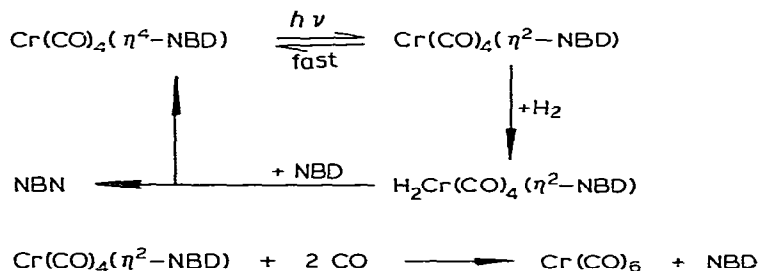
Assuming that the quantum yield for the stoichiometric hydrogenation of the $\text{Cr}(\text{CO})_4(\text{diene})$ complexes are the same for all three dienes ($\phi \approx 0.1$, see above), it must be concluded that for isoprene, and particularly cyclohexadiene, more thermal catalytic cycles accompany each absorption step than in the case of NBD, since the hydrogenation quantum yields are much higher than for NBD. Figure 5 shows that a higher hydrogenation activity (due to more thermal cycles) is accompanied by a larger effect of H_2 pressure. The assumption that increase in number of thermal cycles is responsible for the higher activity in the hydrogenation of CHD is supported by the observation that cyclohexene, for instance, is also formed in the dark periods following irradiation, although at a lower rate.

Discussion

The rates of the photochemical hydrogenations of dienes increases with H_2 pressure, but to different degrees depending on the nature of the diene. We think that two different processes are responsible for this pressure effect. In the hydrogenation of norbornadiene each photochemical primary step is accompanied by only 0 to 3 thermal cycles, as can be seen from the relative low quantum yields; therefore the observed pressure dependence of the NBN formation reflects the reaction of H_2 with the primary photoproduct (*vide infra*). In the case of the conjugated dienes, however, particularly cyclohexadiene, each photochemical step is followed by several thermal cycles. Thus the observed pressure dependence reflects the influence of H_2 on these secondary thermal catalytic cycles. This is verified by the observation that the pressure effect increases with increasing reactivity of the diene (Fig. 4). Thus it is necessary to consider the hydrogenation of norbornadiene and that of the other dienes separately.

Norbornadiene

Previously reported evidence [8,14] and the observed pressure dependence of the norbornene formation, involving increase in the NBN/NTC ratio with increasing H_2 pressure and a decrease in the NBN/NTC ratio with increasing CO partial pressure (see Tables 1 and 2) support a mechanism for the NBN-formation, as summarized in Scheme 2.

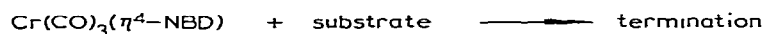
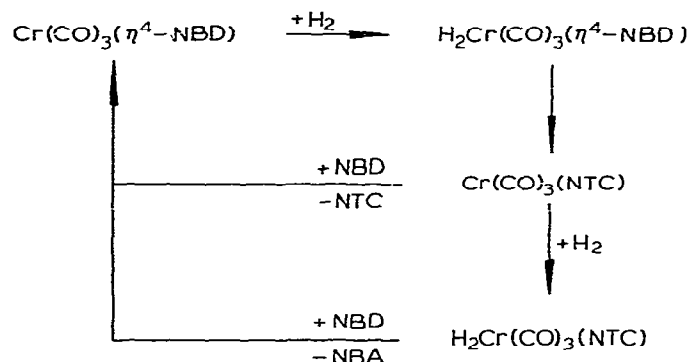
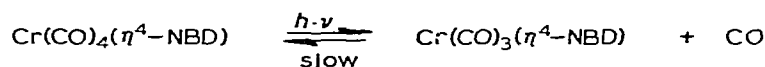


SCHEME 2

On the other hand, the formation of the 1.3-addition product nortricyclene is nearly independent of H_2 pressure.

A zero order reaction with respect to the H_2 -concentration means that the

hydrogen traps all the chromium carbonyl precursors, even at normal pressures. The H_2 concentration at 1 bar partial pressure is of the order of $10^{-3} M$. This implies that the precursor which reacts with the hydrogen has a relative long lifetime (e.g. at least a few microseconds, even if the reaction is fast enough to be diffusion controlled). Following the suggestions made by several authors [11,12,14], a likely candidate for this precursor is $Cr(CO)_3(\eta^4-NBD)$. This would lead to a mechanism for the 1,3-hydrogenation of NBD as summarized in Scheme 3, with $Cr(CO)_3(\eta^4-NBD)$ as the repeating unit in the thermal catalytic cycle. Since the reaction stops when the irradiation source is turned off, and because of the low quantum yield, it is necessary to assume that only few thermal catalytic cycles occur for each photon absorbed. That leads to the question of how the catalytic cycle is terminated.

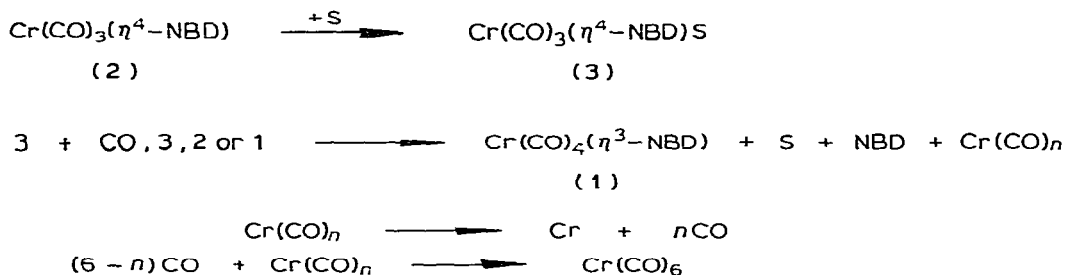


SCHEME 3

The simplest possibility, that of a reaction of $Cr(CO)_3(\eta^4-NBD)$ with the carbon monoxide liberated in the photochemical step, is not very likely, since the CO concentration is extremely low and the results in Table 2 show that added CO has only a moderate retarding effect on the hydrogenation rate.

Other possibilities are trapping by impurities, the catalyst, the initial diene or the product olefin. Since there are, however, no other complexes but $Cr(CO)_4(\eta^4-NBD)$ (1) detectable by IR spectroscopy, the intermediate trapping product must be converted to complex 1 or other species without CO ligands, as indicated in Scheme 4.

The very reactive, coordinatively unsaturated complex 2 reacts first with a substrate S (most likely excess diene or formed monoene) to form a relative labile product 3. Complex 3 may react with free carbon monoxide or may abstract CO from a second molecule 3 or another complex (e.g. 2 or 1). Thus several molecules 3 may be reconverted to 1 for each catalyst molecule destroyed.



(S = NBD, NBN, H₂, impurities etc.; n = 2 or 3)

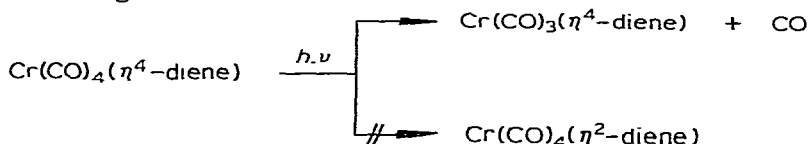
SCHEME 4

The spectra (a) and (b) in Fig. 4 show, that the total concentration of **1** is, indeed, decreased after the hydrogenation is over, and that small amounts of Cr(CO)₆ are formed even in the absence of free CO.

It should be noted that the possibility that norbornene is involved in the termination step was previously considered by Platbrood and Wilputte-Steinert, but in a different connection [8].

Conjugated dienes

For conjugated dienes only 1.4-addition is observed. Using the reasoning above, this means that photochemical excitation of the Cr(CO)₄(η⁴-diene) complex leads exclusively to CO dissociation, without any Cr—diene bond breaking.



This is reasonable, since conjugated dienes are expected to be more strongly bound to the chromium than NBD. Due to the lower energy of the π* orbitals the backbonding between the Cr and the diene is stronger and the backbonding between Cr and CO weaker for the NBD complex than for complexes of conjugated dienes, as can also be seen from the IR stretching frequencies of the carbonyl groups: Cr(CO)₄(η⁴-NBD): 2030, 1959, 1943, 1915 cm⁻¹ [17]; Cr(CO)₄(η⁴-CHD): 2040, 1973, 1952, 1932 cm⁻¹ [4].

We consider that a mechanism analogous to that proposed by Darensbourg *e.a.* (Scheme 2 and 3), which assumes that the "normal" 1.4-hydrogenation of conjugated dienes and the 1.3-hydrogenation of norbornadiene proceed via photochemical dissociation of a CO from the Cr(CO)₄(η⁴-diene) and that the unusual 1.2-hydrogenation of NBD is initiated via a Cr—NBD bond cleavage [14], explains the experimental results obtained in our and previous studies. We are, however, aware that our experiments do not rigorously exclude a mechanism involving only metal—diene bond cleavage, for which evidence has been accumulated by Wilputte-Steinert and coworkers [4,8–10,18].

In this connection it should be mentioned that we were not, for instance, able to detect any evidence of complex **2** by microsecond flash photolysis, and

also that the unusual observed zero order dependence of the NTC formation may be coincidental, e.g. caused by a simultaneous retarding effect of the H_2 pressure in the initial photoreaction and an accelerating effect on the consecutive thermal catalytic cycles. It is further possible that a completely different mechanism, not so far considered, is responsible for the observed effects.

Experimental

$Cr(CO)_6$ and the olefins norbornadiene and isoprene were commercial materials and used after sublimation or distillation, respectively. $Cr(CO)_4(\eta^4\text{-NBD})$ [19] 1,3-pentadiene [20] and cyclohexadiene [21] were prepared according to literature procedures. Products were analysed by gas chromatography on a Carlo Erba Chromatograph with flame ionization detection using a 100 m Ucon LB 550x glass capillary column and methylcyclohexane as internal standard. IR spectra were recorded on a Zeiss IMR-25 and UV-spectra on a Cary 118 spectrometer. Quantum yields were measured with a Fe-oxalat actinometer [22,23]. Monochromatic light was provided with a 1000 W Hg-Xe lamp and a grating monochromator (Schoeffel Instruments).

High pressure hydrogenation experiments: 1 ml of a n-decane solution containing the appropriate concentrations of catalyst, diene and internal GC-standard (methylcyclohexane) were placed in a UV-microautoclave [24]. The solution was flushed 3 times with 10 bar of hydrogen (high purity grade) and then brought to the desired pressure. After the reaction the autoclave was depressurized and the solution analyzed by GC. The light source was a 1000 W Hg-Xe lamp (Schoeffel Instruments) equipped with a pyrex filter cutting off all wavelengths below 290 nm.

Acknowledgement

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