Journal of Organometallic Chemistry, 168 (1979) C13–C15

Preliminary communication

PHOTOCATALYSIS AT ELEVATED PRESSURE: THE CHROMIUM HEXACARBONYL-CATALYZED HYDROGENATION OF NORBORNADIENE

MANFRED J. MIRBACH, DIETER STEINMETZ and ALFONS SAUS

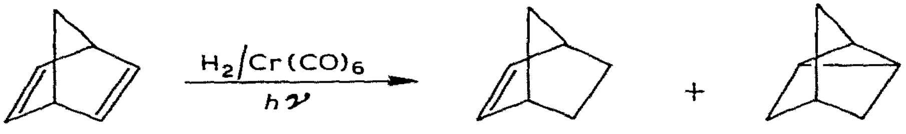
Institut für Technische Chemie und Petrolchemie, RWTH Aachen, Alte Maastrichter Str. 2, D-5100 Aachen (West-Germany) and F.B. 6, "Angewandte Chemie" Gesamthochschule Duisburg, Lotharstrasse 55, D-4100 Duisburg (West-Germany)

(Received December 12th, 1978)

Summary

The photo-catalysed hydrogenation of norbornadiene in the presence of chromium hexacarbonyl has been studied at pressures of up to 80 Bar. The norbornene/nortricyclene ratio increases considerably with increasing pressure; at and above 40 Bar both double bonds of norbornadiene are hydrogenated, to give norbornane.

The selective 1,4-hydrogenation of dienes to *cis*-monoenes catalyzed by $Cr(CO)_6$ is one of the "classical" photocatalysed reactions [1–3]. Norbornadiene (NB) differs from most other dienes in giving two hydrogenation products, norbornene (NN) and nortricyclene (NT) [4,5].



(NB) (NN) (NT)

We investigated this reaction at hydrogen pressures up to 80 Bar in a modified UV-autoclave [6]*. Three major changes in behaviour from that at normal pressure are apparent from our results, which are listed in Table 1.

(a) The conversion of norbornadiene and the formation of norbornene increase with increasing hydrogen pressure, following approximately first order kinetics.

---

*The autoclave was equipped with 6 separately stirred Pyrex test tubes each containing 2 ml of solution. The values given are averaged over 3 runs. The systematic error is ± 10%

TABLE 1

PHOTOCHEMICAL HYDROGENATION OF NORBORNADIENE AT ELEVATED HYDROGEN PRESSURE

Catalyst: $Cr(CO)_6$, 3.6×10^{-3} mol l^{-1}; [NB] 0.14 mol l^{-1}; solvent: n-decane; lamp: HPK 125; reaction time: 1 h; temperature 25° C

$P(H_2)$ (Bar)	NB[a] (mmol l^{-1})	NN[b] (mmol l^{-1})	NT[c] (mmol l^{-1})	NT/NN	NA[d] (mol l^{-1})
1	91	11	37	3.4/1	—
5	73	19	41	2.2/1	—
40	40	46	42	1/1.1	6
80	35	53	37	1/1.4	14

[a] Norbornadiene. [b] Norbornene. [c] Nortricyclene. [d] Norbornane.

(b) The product ratio NT/NN changes dramatically from 3.4/1 at 1 Bar to 1/1.5 at 80 Bar hydrogen pressure.

(c) At pressures ≥ 40 Bar both double bonds of norbornadiene are hydrogenated, to give norbornane.

The first effect, the increase in the reaction rate is expected, since Platbrood and Wilputte-Steinert found the reaction to be 1st order with respect to

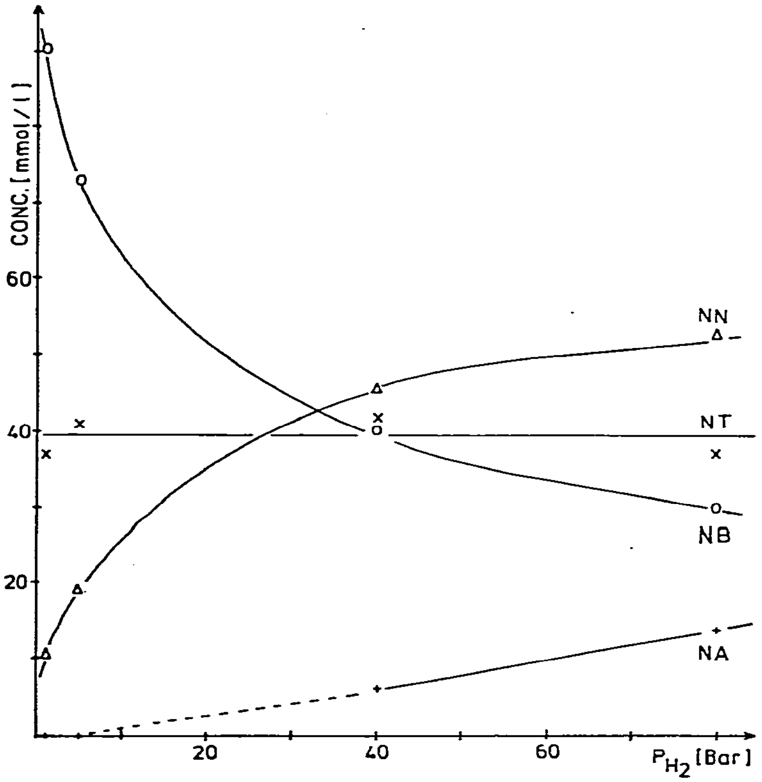


Fig. 1. Photochemical hydrogenation of norbornadiene at various hydrogen pressures. —○—○—NB: concentration of norbornadiene; —△—△—NN: concentration of norbornene; —X—X—NT: concentration of nortricyclene; —+—+—NA: concentration of norbornane (mmol l^{-1}) after 1 h of irradiation.

hydrogen at pressures below 360 Torr [4]. The other two effects are rather surprising since they are the opposite of those previously assumed [4,8].

To check whether the observed effects are due to an increase in hydrogen concentration or to an exceptionally large negative activation volume, the hydrogenation was carried out at a constant H_2-pressure of 5 Bar and various pressures of nitrogen. In these experiments no significant change in product ratio was observed, and a small fall in the reaction rate with increasing nitrogen pressure was probably due to quenching by impurities in the nitrogen. Thus the increase in hydrogen concentration is the crucial factor in our experiments.

It is important to note that the change in the product ratio is due only to the enhanced formation of norbornene, the rate of formation of nortricyclene being independent of the pressure.

None of the reaction mechanisms previously proposed [4,7,8] explains our results satisfactorily. The observed effects require that two separate catalytic cycles operate in the photocatalyzed hydrogenation of norbornadiene. One, which is independent of H_2-concentration, leads to the formation of nortricyclene, and the other, the rate-determining step of which is first order with respect to hydrogen concentration, produces norbornene. We hope that further investigation will lead to new insight into the still somewhat controversial reaction mechanism, and to preparative applications of the pressure method in photocatalysis.

References

1 J. Nasielski, P. Kirsch and L. Wilputte-Steinert, J. Organometal. Chem., 27 (1971) C13.
2 M. Wrighton and M.A. Schroeder, J. Amer. Chem. Soc., 95 (1973) 5764.
3 G. Platbrood and L. Wilputte-Steinert, J. Organometal. Chem., 70 (1974) 407.
4 G. Platbrood and L. Wilputte-Steinert, J. Organometal. Chem., 70 (1974) 393.
5 G. Platbrood and L. Wilputte-Steinert, Bull. Soc. Chim. Belg., 82 (1973) 733.
6 A. Saus, C.Z.-Chemie-Technik, 2 (1973) 19.
7 M.A. Schroeder and M.S. Wrighton, J. Organometal. Chem., 74 (1974) C29.
8 D.J. Darensbourg, H.H. Nelson, III and Mark A. Murphy, J. Amer. Chem. Soc., 99 (1977) 896.