Kinetic study of the addition reaction of carbon tetrachloride to 1-hexene initiated by chromium hexacarbonyl in the presence of UV light

A Harfoush

Atomic Energy Commission of Syria, Department of Chemistry, Damascus, P.O. Box 6091, Syria

Email: aharfoush@aec.org.sy

Received 11 January 2005; revised 18 April 2005

Addition reaction of CCl₄ to the double bond of olefin (particularly 1-hexene) in the presence of Cr(CO)₆ and light has been investigated. The reaction follows, mainly, a free radical chain route in which the metal complex acts solely as an initiator. The observed orders of reaction clearly demonstrate that the reaction proceeds by a free radical chain route. The effect of UV light has been studied and found to be responsible for the initiation of the free radical chain process and for the preparation of photocatalytic species, which are photolabile and responsible for the formation of a small amount of the addition reaction product during the dark periods. Cr(CO)₆ shows initiation efficiency comparable with organic peroxides, but other complexes, Mo(CO)₆, W(CO)₆, are less efficient.

IPC Code: Int. Cl.7 C07B37/02

The Kharasch reaction, i.e., the addition of polyhaloalkanes to olefins, is a well-known method for the formation of a C-C bond. This type of addition reaction is undoubtedly a significant reaction from the synthetic viewpoint. Understanding the mechanism is a key factor for the development of an efficient catalytic asymmetric synthesis for the preparation of a wide number of optically active organic compounds. The organic peroxides initiate the addition reaction of halocarbons to alkenic double bonds (the Kharasch addition reaction) by a free radical chain mechanism. Some low-valence transition metal complexes (TMC) catalyze this type of reaction. The mechanism of the catalysis of this addition reaction by TMC is still in debate.

Different mechanisms have been suggested at various stages of investigation of the thermal TMC-catalyzed Kharasch reaction. Tararov et al. summarized the possible mechanisms for this reaction as: (i) A classical radical chain reaction in which the metal acts simply as an initiator for the production of R*R from RX followed by the formation of adduct radical R*A as a result of the addition of R to the olefin. A chain transfer R*R is initiated by the attack of the adduct radical to RX via an abstraction of a halogen atom; (ii) A redox-catalytic mechanism, which differs from the previous one in that the chain transfer is accomplished by the transfer of a halogen from MX to the adduct radical; (iii) A modified redox-catalytic mechanism in which a pairing of R with metal ion takes place and in the presence of olefin a pairing of R*A and metal ion occurs by the formation of the addition product, R*A X, by the transfer of the halogen atom to the adduct radical; and, (iv) A metal complex mechanism that involves an oxidative addition of RX to M which gives rise to the RMX species, followed by the insertion of an olefin into the R-M bond and the reductive elimination of the addition product with regeneration of the catalytic complex (Scheme 1).

Photochemistry offers a simple, and often highly selective, route to organic compounds, overcoming large enthalpy barriers. As a consequence, it is often possible to synthesize compounds that otherwise demand harsh conditions in conventional thermochemical routes. It is also possible to prepare homogeneous catalysts having unsaturations of coordination as active intermediate species far more efficiently and rapidly using photochemistry as compared to thermochemistry.

This would present an alternative route for promoting the Kharasch addition of CCl₄ to alkenes [Eq. 1 (Scheme 2)].

Detailed mechanistic studies have not been conducted on such reactions in the presence of M(CO)₆ and light.

In another work, our general aim was to explore the use of light in the presence of 6th group metal carboxyls, (Cr(CO)₆, Mo(CO)₆ and W(CO)₆), as an alternative route for the possible transformation of
linear and cyclic olefins in the presence of CCl₄. Among these carbonyls, Cr(CO)₆ was the most powerful complex to achieve the highest selectivity (>99%) and complete reaction of the addition of CCl₄ to the olefins.

The aim of this study was to carry out a kinetic study on the reaction of CCl₄ addition to 1-hexene in the system Cr(CO)₆/CCl₄/1-hexene/hv, in order to determine the role of light and to elucidate the mechanism of this addition reaction.

Materials and Methods
All used tools such as syringes, needles, distillation systems, tubes and flasks were washed, rinsed with acetone, dried in an oven for 3 h at 110°C and cooled under dry oxygen-free nitrogen atmosphere before use.

CCl₄ and toluene (UV spectroscopic grade), supplied by s.d. Fine-Chem. Ltd and SRL, respectively, isoctane (GR, Merck) and 1-hexene (supplied by Aldrich) were dried, degassed and distilled under dried oxygen-free nitrogen. Particular
care was taken to secure that organic reagents were free from peroxide impurities. Toluene was used as solvent in the experiments where concentration of CCl$_4$ was varied to have the total volume of the solution at 20 mL. Isooctane was used as internal standard. In separate experiments, toluene and isooctane were shown to be unaffected by irradiation with either Cr(CO)$_6$ or CCl$_4$. Chromium hexacarbonyl was supplied by Aldrich and used without any treatment. The photolysis reaction was carried out in a photochemical reactor (Heber Scientific HEAOP System) using 350 nm wavelength low-pressure mercury lamps as a light source.

Transfer of solvents and all other manipulations were carried out with rigorous attention to exclude air contamination. The reactions were carried out in a two-neck glass tube (with a height of 15 cm and an inner diameter of 2 cm) equipped with an inner refrigerated system, rubber septum and a Teflon coated magnet to ensure cooling and stirring during irradiation. Table 1 shows the different operational techniques used during this work.

Carbon tetrachloride (29.41 g, 0.286 mol), 1-hexene (0.83 g, 9.9x10$^{-3}$ mol), 0.32 mL isooctane and chromium hexacarbonyl (1.44x10$^{-4}$ mol) were loaded into the tube, which was already enveloped with aluminum sheet. The solution was stirred for 10 min to dissolve the metal carbonyl then the response factor was measured four times. Afterwards the tube was fixed in the center of a photochemical reactor. The UV lamps were activated 1 h ahead of the start of the reaction in order to obtain a stabilized light intensity. The irradiation of the solution was maintained until the concentration of the addition reaction product attained a fixed value. The solution was subjected, during irradiation, to a continual stirring and constant temperature (20°C). Samples were taken every 17 min and analyzed by the GC technique. The conversion percentage of final products of the addition reaction is defined as:

$$\text{Conversion (\%)} = \frac{\text{number of moles of formed product}}{\text{number of moles of departure olefin}} \times 100$$

**Analyses of samples**

Samples were taken at regular intervals of time to be analyzed immediately by using Nucon 5700 Gas Chromatograph equipped with a 2m, 10% SE 30 on Chromosorb W 100-120 mesh, column (column temperature: 50-250°C at a rate of 16 °C/min; injector: 250°C; detector: 280°C; nitrogen flow rate: 30 cm$^3$ min$^{-1}$).

Identification of the addition product and secondary products was made by (GCMS-QP5000, Shimadzu; GC-17A, Shimadzu; Wiley 139.Lib). NMR, 200 MHz, BRUKER, was also used to identify the addition product, after isolation of the product.

**Results and Discussion**

**Role of light**

It is not easy to evaluate the role of light in the formation of the addition products and to give a classification of the possible various reactions. Due to the different operational techniques of irradiation (Table 1), one could elucidate some important observations.

In the absence of 1-hexene, Cr(CO)$_6$/CCl$_4$ solution was irradiated for 30 min. Then, in the absence of light, 1-hexene was added to the irradiated solution. Analysis of this mixture proved the absence of any addition products.

We studied the transformation of the olefin to the corresponding tetrachlorinated hydrocarbons in the system Cr(CO)$_6$/1-hexene/CCl$_4$ (Fig. 1) with continual and sequential (succession of irradiation phases (irradiation periods) and thermal phases (dark periods) irradiations.

Figure 1 shows the behaviour of 1-hexene by tracing the conversion in addition product during the continual and sequential irradiations. The reaction

<table>
<thead>
<tr>
<th>Technique of irradiation</th>
<th>Possible reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continued</strong></td>
<td>Promoter and substrate are submitted to a continued irradiation which gives photoassisted and photocatalyzed reactions</td>
</tr>
</tbody>
</table>

(Promoter + Substrate) | Irradiation phase | Thermal phase |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequential</td>
<td>Photoassisted and photocatalyzed reactions</td>
<td>Photocatalyzed reaction</td>
</tr>
</tbody>
</table>
may be complete if irradiation time is long enough. Thus, after 12 h of irradiation, the system Cr(CO)₆/1-hexene/CCI₄ leads to the formation of 97.4% of the expected addition product.

Comparison of the two procedures of irradiation shows clearly that conversion of the olefin is directly related to the presence of light.

The essential result is that the addition reaction of CCl₄ on the olefin is produced not only during the phases of irradiation but also during the dark periods (Fig. 1). However, in the dark period, the reaction speed is highly reduced. We may, thus, conclude that the addition reaction proceeded simultaneously in photoassisted (i.e., formation of addition product in the presence of light) and photocatalytic (i.e., formation of addition product in the absence of light) processes.

In order to evaluate the relative importance of the two types of processes, the relative activities of the catalytic system in the presence and absence of light as a function of time is presented in Table 2. It shows that the contribution of the photocatalytic and photoassisted processes to the entire formation of addition product is in the order of 2.3-7.5% and 92.5-97.7%, respectively (Table 2). The results also prove that these activities diminish with the increase in "tₚ" (time of irradiation), indicating that the species responsible for the activity in the absence of light are photolabile.

Thus, it could be concluded that the formation of the addition reaction product in a dark period, during the sequential irradiation, is presumably due to the presence of catalytic species. The formation of these species, such as Cr(CO)₆L₃ (L = olefin, Cl or CCl₄), proposed by Gandolfi and Cais, could be generated photochemically during a preceding period of irradiation. The mechanism, in this case, involves oxidative addition of CCl₄ to the metal, followed by olefin insertion into the M-CCl₃ bond. The cycle is then completed by reaction of the alkylmetal with a further molecule of CCl₄, thereby forming the product by chain sequence [Eq. (IV) in Scheme 1].

However, it is noteworthy, that, following the disappearance of Cr(CO)₆ and the evolution of CO during the irradiation of Cr(CO)₆/olefin/CCI₄ system, the value of α (number of evolved CO moles per mole of transformed Cr(CO)₆) is 3, which is consistent with the proposed formula [Cr(CO)₅L₃].

Side products

Precise analysis of Cr(CO)₆/1-hexene/CCI₄/hv solution indicated the presence of C₅Cl₅, CHCl₃, C₆H₄Cl₂ and C₆H₃Cl₄ as side products. We observed that the formation of C₅Cl₅ and CHCl₃ has ceased immediately after irradiation was stopped.

Trichloromethyl radical was generated photochemically following the classical mechanism [Eq. 2 (Scheme 2)].

The presence of radicals in the reaction medium, specially the presence of °CCI₄, is confirmed by elucidating the side products, some of which corresponds to the chain terminal steps. Thus, C₅Cl₅ is the result of the combination of two trichloromethyl radicals. The formation of C₆H₂Cl₄ may be explained by [Eq. 3 (Scheme 2)].

Table 2 — Addition reaction of CCl₄ on 1-hexene in Cr(CO)₆/CCI₄ in sequential irradiation (see Fig. 1).

<table>
<thead>
<tr>
<th>Phase No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequential irradiation</td>
<td>hv</td>
<td>Δ</td>
<td>hv</td>
<td>Δ</td>
<td>hv</td>
<td>Δ</td>
<td>hv</td>
</tr>
<tr>
<td>Time duration (min)</td>
<td>30</td>
<td>36</td>
<td>42</td>
<td>54</td>
<td>48</td>
<td>128</td>
<td>48</td>
</tr>
<tr>
<td>Relative activity of addition reaction</td>
<td>100</td>
<td>7.5</td>
<td>35.0</td>
<td>2.2</td>
<td>16.8</td>
<td>0.4</td>
<td>10.0</td>
</tr>
</tbody>
</table>

hv: UV irradiation; Δ: thermal; *: arbitrary value of addition production during 30 min.
The production of chloroform certainly comes from an abstraction of hydrogen [Eq. 4 (Scheme 2)].

In comparison with addition reaction (selectivity >99%), the incidence of hydrogen abstraction is much less, possibly due to the higher energy needed for activation of the process.

The formation of C₆H₁₁Cl₂ may, for example, be envisaged as an attack of °Cl radical on the olefin.

**Kinetics studies**

There are no previous reports on the use of metal carbonyls and light to promote reactions of this type. However, Cr(CO)₆ was used to perform this reaction thermochemically, at a relatively harsh conditions (120°C), all be it, with less effective conversion.

Since the participation of the photocatalytic process in the formation of the addition product is relatively low, and due to the practical difficulty faced trying to explain this process so far, we proceeded to a kinetic study concerning the formation of addition product during a continual irradiation.

In our mechanistic study of Kharasch addition reaction in the presence of Cr(CO)₆, we chose to study the reaction of 1-hexene with tetrachlorocarbon, [Eq. 5 (Scheme 2)].

The product of this reaction is 1,1,1,3-tetrachloroheptane, a compound that can be analyzed by gas-liquid chromatography relatively rapidly.

Reactions of this type have already been shown in the presence of organic peroxides following free radical chain mechanisms.

This addition reaction could not be initiated in the absence of light and/or metal carbonyls even at 60°C.

In view of the high performance of the chromium carbonyl-promoted reaction described above, we conducted a detailed study of the photoassisted reaction mechanism.

The initial rate method was used and this involved varying the concentration of one component while maintaining the other two constant carried out the kinetic study. The total volume of the reaction mixture was kept constant during studies of the effects of variation of 1-hexene and CCl₄ by adding appropriate amount of toluene and isooctane (isooctane was taken as internal standard for the analysis by GC technique). Control reactions showed that toluene and isooctane did not react with any combination of reagents and the metal carbonyl.

Figures 2, 3 and 4 show the variation of the initial rate of reaction plotted against [Cr(CO)₆]¹², [CCl₄]¹².

Fig 2 — Initial reaction rate versus Cr(CO)₆.

Fig 3 — Initial reaction rate versus CCl₄.

Fig 4 — Initial reaction rate versus 1-hexene.
and [1-hexene], respectively. In each case a good linear plot was obtained. It should be noted that there is a small positive intercept to Figs 2-4, which is in accord with the findings discussed above, that there is a small contribution from a reaction which is not promoted by Cr(CO)$_6$. For this reason, no attempt was made to obtain activation parameters for the reaction.

It is, however, possible to obtain values for the second order rate coefficient, $k$, as defined in the rate expression:

$$\text{Rate} = k[\text{Cr(CO)}_6]^{1/2}[\text{CCl}_4]^{1/2}[\text{1-hexene}]$$

Values of $(3.54 \pm 0.15) \times 10^{-4}$, $(3.53 \pm 0.15) \times 10^{-4}$ and $(3.58 \pm 0.15) \times 10^{-4}$ mol$^{-1}$ s$^{-1}$ were obtained from studies of the variation in concentrations of Cr(CO)$_6$, CCl$_4$ and 1-hexene, respectively.

In view of the fact that these values were obtained employing the initial rate method, which can be subject to considerable error due to the difficulty in estimating the correct tangent to the rate curve, the agreement between them is satisfactory.

The appearance of a fractional order in the rate expression suggests the existence of a free radical chain reaction mechanism$^{18}$ [Eq. (1) in Scheme 1].

Qualitative extrapolation to other olefins and promoters

Under the same experimental conditions, in a qualitative study, we investigated the addition reaction of the system Cr(CO)$_6$/CCl$_4$ in the case of 1-butene, 1-pentene and 1-heptene which convert respectively to the tetrachloro-1,1,1,3-pentane, tetrachloro-1,1,1,3-hexane and tetrachloro-1,1,1,3-octane.

On the other hand, the addition reaction may be initiated by light in the presence of other derived carbonyls of transition elements. 1-hexene, with Mo(CO)$_6$ and Fe(CO)$_3$ after 2 h of irradiation, under identical experimental conditions produced tetrachloro-1,1,1,3-heptane as the addition product in 4% and 28% yield, respectively. W(CO)$_6$ leads simultaneously to metathesis reaction of 1-pentene and polymerization of norbornene, in addition to addition products with very low selectivity.

Acknowledgement

Sincere thanks are due to the Third World Academy of Sciences (TWAS) for sponsoring a TWAS Associateship Scheme in India. Prof. B. Viswanathan, Prof. G. Sundrarajan, Prof. A. Chadha and other members of the IIT-Madras, are thanked for their valuable help. Prof. I. Othman, Director General of the Atomic Energy Commission of Syria, is thanked for his persistent encouragement.

References