Russian Journal of General Chemistry, Vol. 75, No. 5, 2005, pp. 734–738. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 5, 2005, pp. 778–782.
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Addition of Tetrachloromethane to Alkenes, Catalyzed by Pt(II) Complexes

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Received December 26, 2003

Abstract—Platinum(II) complexes [dichlorobis(triphenylphosphine)platinum(II), dichlorobis(tri-*m*-tolylphosphine)platinum(II), dichloro(2,9-dimethyl-1,10-*N,N'*-phenanthroline)platinum(II), etc.] showed catalytic activity in addition of tetrachloromethane across the double bond in 1-hexene, 1-heptene, 1-octene, 1-decene, and cyclohexene. The stability of the platinum catalysts was evaluated by GLC, gas chromatography–mass spectrometry, and ^{31}P NMR and IR spectroscopy; the kinetic relationships of the addition reactions were determined. A reaction mechanism involving formation of trichloromethyl radical was suggested. A correlation was revealed for the first time between the catalytic activity of platinum, palladium, and rhodium complexes and the capability of these complexes to generate hexachloroethane.

The addition of tetrachloromethane to alkenes can be effected by free-radical initiatiors [1] or by transition metal salts and complexes [2–4]. As a rule, the reaction products in this case are not only 1 : 1 adducts but also telomeric homologs [1, 5]. With organic peroxides used as initiators of tetrachloromethane addition, the necessary condition for obtaining the 1 : 1 adduct is a 7–10-fold excess of tetrachloromethane relative to alkene [1]. In the case of using coordination catalysts, tetrachloromethane is also taken in excess (usually fivefold) to increase the yield of the target product [3, 6].

We have found previously [7] that Pt(II) complexes show high activity in addition of tetrachloromethane to alkenes. In particular, the reaction performed in the presence of $PtCl_2(PPh_3)_2$ gives the 1 : 1 adduct as the major product in a high yield. As compared to the known catalytic systems for Kharasch addition, the system that we developed has certain advantages. In particular, with Co(II) [3] and Cu(I) [2] as catalysts, CCl_4 was taken in a large excess relative to the alkene [(5–10) : 1]. In the presence of Pt(II) phosphine complexes, the addition is very selective at 1.3 : 1 molar ratio of CCl_4 to the alkene. The catalytic system based on $PtCl_2(PAr_3)_2$ preserves the activity for several tens of hours. In contrast to the known catalysts, e.g., to those based on transition metal carbonyls [8], the Pt(II) complexes are stable under the reaction conditions for a long time. Also, the addition is effected at a catalyst concentration as low as 0.06–0.50 mol %, which is more than an order of magnitude lower than the necessary concentrations of the catalysts containing Re(III) (2 mol % [4]) and Co(II) (16 mol % [3]).

As a model substrate we chose hexene. Although the Pt(II) complexes catalyze the addition of CCl_4 to 1-hexene in a wide temperature range (67–140°C), we chose the temperature of 120°C for consistency.

We found that *cis*-$PtCl_2(PPh_3)_2$ (**I**), $PtI_2(PPh_3)_2$ (**II**), $PtI_2(COD)$ (**III**) (COD = 1,4-cyclooctadiene), $PtCl_2[P(m\text{-Tol})_3]_2$ (**IV**), $PtMe_2(PPh_3)_2$ (**V**), and $PtCl_2 \cdot (2,9\text{-}Me_2phen)$ (**VI**) (2,9-Me_2phen = 2,9-dimethyl-1,10-*N,N'*-phenanthroline) catalyze the addition, with 1,1,1,3-tetrachloroheptane **VII** being the major product. $PtCl_2(COD)$ shows no appreciable catalytic activity in this reaction. Data on the catalytic activity of the Pt(II) complexes used are given in Table 1.

The highest yields of the adducts were attained with complexes **II** and **V**. However, these complexes are unstable under the reaction conditions: at 120°C within 2 h they virtually fully transform into $PtCl_2 \cdot (PPh_3)_2$.

In contrast to iodides **II** and **III**, platinum(II) chloride triarylphosphine complexes **I** and **IV** preserve their activity even at high olefin conversions. We examined the solid residues isolated after heating **I** at 120°C for 10.5 h in the mixtures CCl_4–CH_3CN–1-hexene (sample 1), CCl_4–CH_3CN (sample 2), and 1-hexene–CH_3CN–C_6H_6 (sample 3). The IR spectra of all these samples contain two bands at 320 and 294 cm^{-1}, corresponding to the starting *cis*-$PtCl_2 \cdot (PPh_3)_2$ [9].

In the ^{31}P NMR spectra of samples 1–3, the signals of the starting *cis*-dichlorobis(triphenylphosphine)-platinum at 14.8–14.9 ppm, with two platinum satellites ($^1J_{PtP}$ 3671–3673 Hz) are preserved. Also, a number of new signals of phosphorus-containing species appear in the spectra of samples 1 and 2. Their total integral intensity does not exceed 15% of that of *cis*-$PtCl_2(PPh_3)_2$ in sample 1 and 45% in sample 2. We failed to detect the platinum satellites for these signals, probably because of their low intensity.

The reaction order with respect to the catalyst was determined with complex **I**, which was the most stable under the reaction conditions; its concentration was varied from 5.0×10^{-4} to 4.2×10^{-3} M. The reaction orders with respect to CCl_4, 1-hexene, and CH_3CN were determined by replacing the reagent by an inert diluent (benzene). The initial reaction rate was determined at the 1-hexene conversion not exceeding 1%. The rate of the noncatalytic reaction [$(1.3 \pm 0.2) \times 10^{-6}$ mol l^{-1} s^{-1}] is an order of magnitude lower than that in the presence of *cis*-$PtCl_2(PPh_3)_2$ [$(17 \pm 1) \times 10^{-6}$ mol l^{-1} s^{-1}]. Therefore, in the further kinetic studies, the contribution of the noncatalytic process in the presence of **I** was neglected.

We found that the reaction is second-order with respect to tetrachloromethane, zero-order with respect to 1-hexene, and first-order with respect to the Pt(II) complex. Also, it has a nonzero order with respect to acetonitrile. A complex effect of acetonitrile additions on the activity of Pt(II) phosphine complexes in the presence of tetrachloromethane was observed previously [10].

We found that additions of benzoquinone inhibit the reaction, which, apparently, suggests the radical reaction mechanism. The reaction inhibition with triphenylphosphine, most likely, suggests formation of an active 14-electron platinum complex by reversible dissociation of the ligand [11, 12].

Addition of K_2CO_3 to the reaction mixture CCl_4–1-hexene (1.3 : 1) increases both the reaction rate and the yield of the 1 : 1 adduct (from 13 to 52% at 120°C, 10.5 h). At the CCl_4–1-hexene molar ratio of 3.9 : 1, the yield under the same conditions is 78%, and in 24 h it approaches 100% (the reaction mixture, according to gas chromatography–mass spectrometry, does not contain even traces of 1-hexene). The effect of potassium carbonate may be associated with the formation of more active Pt(0) complexes, as it was assumed previously for the systems containing tetrachloromethane and Pd(II) and Pt(II) phosphine complexes [4, 13, 14].

All the catalytic systems based on Pt(II) complexes that we tested showed high selectivity in addition of tetrachloromethane to 1-hexene. An examination by gas chromatography–mass spectrometry revealed no detectable amounts of telomers or 1,1,1-trichloro-2-chloromethylhexene (anti-Markownikoff adduct).

Table 1. Catalytic activity of Pt(II) complexes in addition of tetrachloromethane to 1-hexene in the presence of acetonitrile (1 : 1 : 1 by volume, 120°C)

Catalyst no.	Catalyst	$k \times 10^3$, l^2 mol^{-2} s^{-1}	V_0/[Pt] $\times 10^3$, s^{-1}
I	*cis*-$PtCl_2(PPh_3)_2$	1.19 ± 0.08	4.1 ± 0.3
II	$PtI_2(PPh_3)_2$[a]	0.63 ± 0.05	2.2 ± 0.2
III	$PtI_2(COD)$[a]	0.13 ± 0.01	0.45 ± 0.03
IV	*cis*-$PtCl_2 \cdot [P(m\text{-}CH_3C_6H_4)]_2$	0.083 ± 0.002	0.286 ± 0.007

[a] Catalysts **II** and **III** are unstable under the reaction conditions and transform into the corresponding dichloride complexes within 2 h; for **II** and **III**, the rate constant in the initial step of the reaction is given.

As possible side processes we can consider isomerization of 1-hexene and metathesis of C–H bonds in the alkene and C–Cl bonds in CCl_4.

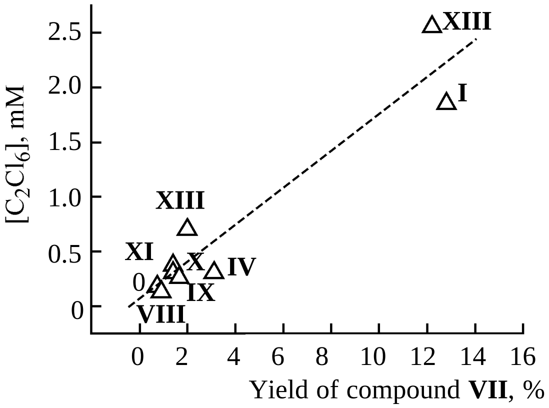
The Pt(II) complexes studied are not active catalysts of alkene isomerization under the reaction conditions. Only cyclooctadiene complexes **III** and **VIII** showed some activity in isomerization of 1-hexene. In particular, about 1/3 of 1-hexene is converted to a mixture of *cis*- and *trans*-2-hexene at 120°C in 10 h.

Since Pt(II) and Pd(II) complexes can catalyze the metathesis of the C–H bonds in alkanes and C–Cl bonds in CCl_4 [10], such a process could be expected with 1-hexene along with the addition. Indeed, the most active allylic C–H bonds undergo metathesis with the formation of 3-chloro-1-hexene and *cis*- and *trans*-1-chloro-2-hexene. We found, however, that the metathesis rate is lower than the addition rate by two orders of magnitude.

Thus, the catalytic systems based on Pt(II) phosphine complexes are highly selective. The content of by-products in the reaction mixtures under consideration is two orders of magnitude lower than that of the addition product, even at a high (>50%) conversion of the alkene.

The addition involving Pt(II) complexes may occur along two alternative pathways. The plausible initial step of the first pathway is activation of the alkene with the formation of a Pt(II) π complex, and that of the second pathway, activation of the C–Cl bond in CCl_4 with the formation of, e.g., a new complex with a Cl–Pt(II) bond.

The mechanism involving the coordination of the



Correlation between the concentration of hexachloroethane in the CCl_4–CH_3CN system and yield of the addition product in the 1-hexene–CCl_4–CH_3CN system (10.5 h, 120°C).

olefin with Pt seems improbable, in view of the zero reaction order with respect to the alkene. Furthermore, platinum alkene complexes were detected neither upon prolonged heating of the complexes in 1-hexene nor in reaction mixtures.

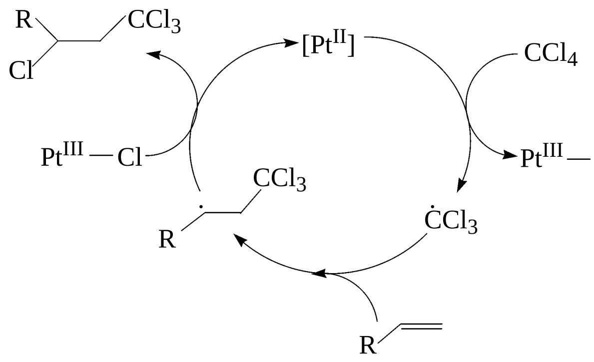
On the contrary, the mechanism of redox catalysis involving the abstraction of a chlorine atom from tetrachloromethane by a metal complex with the formation of trichloromethyl radical is quite typical of catalytic systems based on many transition metals, e.g., Pd(II) [15], Fe(II) [16], Cu(I) [2], and Co(II) [3]. Previously we obtained evidences of formation of trichloromethyl radical in chlorination of hydrocarbons with tetrachloromethane in the presence of Pt(II) phosphine complexes [10, 17].

As the CCl_4 concentration is decreased, the relative amount of by-products compared to the addition product increases: At a tenfold decrease in the CCl_4 concentration, the concentrations of the other components being constant, the relative amount of the metathesis products increases by a factor of 4. Lower selectivity of the reaction at low concentrations of tetrachloromethane can lead to a higher formal order with respect to CCl_4.

Another possible cause of the increase in the reaction order with respect to CCl_4 is the influence of tetrachloromethane on the release of the phosphine from the Pt(II) 16-electron complex. It is known that CCl_4 reacts with triphenylphosphine to form $[Ph_3PCCl_3]^+Cl^-$ and other reaction products [18]. This reaction is fast in the presence of acetonitrile; in nonpolar solvents, its rate is low. If such a reaction facilitates formation of the active catalyst species, then, presumably, a decrease in the concentration of tetrachloromethane will cause a stronger decrease in the reaction rate than it could be expected from the classical scheme of redox catalysis.

The detection of dichloroethane, the dimerization product of the trichloromethyl radical, could be an additional evidence of the participation of this radical in the process. However, hexachloroethane was not detected in the reaction mixtures containing alkenes. The absence of dimerization products in radical reactions, including the Kharasch reaction, was reported previously and was interpreted in [19]. We attempted to detect hexachloroethane in a CCl_4–CH_3CN mixture in the absence of 1-hexene. Upon heating of this mixture to 120°C, we detected by gas chromatography–mass spectrometry the formation of hexachloroethane both in the absence of transition metal complexes and in the presence of various Pt, Pd, and Rh complexes. The formation of hexachloroethane is accelerated in the presence of complexes catalyzing the Kharasch reaction. Furthermore, the catalytic activity of these complexes correlates with their capability to generate hexachloroethane (correlation factor 0.95). These data are shown in the figure [**IX**, $PtCl_2(Ph_2PCN)_2$; **X**, $PdCl_2(Quin)_2$ (Quin is quinoline); **XI**, *trans*-$PtCl_2 \cdot (SMe_2)_2$; **XII**, $PdCl_2(\beta\text{-Pic})_2$ (β-Pic is 3-methylpicoline); **XIII**, $RhCl(PPh_3)_3$; 0, noncatalytic reaction]. Such a correlation was not described previously.

Thus, our results allow us to suggest the following catalytic cycle of the addition of CCl_4 to 1-hexene in the presence of *cis*-$PtCl_2(PPh_3)_2$ (see scheme). In this scheme, $[Pt^{II}]$ denotes complex **I** or a complex formed by elimination of phosphine from **I**. The active catalyst species participates in the formation of the trichloromethyl radical, with an increase in the Pt oxidation state. The trichloromethyl radical adds to the double bond, and the resulting radical adduct abstracts the chlorine atom from the oxidized platinum species, with the formation of the addition product and regeneration of the catalyst. The suggested scheme coincides with the mechanism of redox catalysis.



We have studied the activity of $PtCl_2(PPh_3)_2$ in reactions with various alkenes (Table 2). As expected, the addition occurs faster with terminal alkenes. It is interesting that, in the reaction with cyclohexene, the ratio of the *cis* and *trans* products of CCl_4 addition appeared to be close to 1 : 1 (random addition), which also indirectly suggests the radical mechanism [3, 4].

Thus, Pt(II) complexes show a high catalytic activity in addition of CCl_4 to C=C double bonds. The catalytic system based on Pt(II) triarylphosphine complexes allows preparation of the addition products in quantitative yields at a low molar ratio of tetrachloromethane to alkene and low concentration of the catalyst. We found that the catalyst preserves its activity in the process for a long time and can be reused.

Table 2. Rate constants of addition of tetrachloromethane to various alkenes in the presence of *cis*-$PtCl_2(PPh_3)_2$, 120°C

Alkene	$k \times 10^3$, $l^2\ mol^{-2}\ s^{-1}$	$V_0/[Pt] \times 10^3$, s^{-1}
1-Hexene	1.19 ± 0.08	4.1 ± 0.3
1-Heptene	0.97 ± 0.05	3.4 ± 0.2
1-Octene	0.97 ± 0.03	3.3 ± 0.1
1-Decene	0.78 ± 0.03	2.68 ± 0.09
Cyclohexene	0.15 ± 0.02	0.53 ± 0.06

EXPERIMENTAL

Tetrachloromethane (pure grade), acetonitrile (chemically pure grade), and benzene (chemically pure grade) were purified by standard procedures [20]. The alkenes were distilled from sodium just before preparing the reaction mixtures. The reactant purity was checked by GLC or gas chromatography–mass spectrometry (GC–MS). The platinum complexes were prepared by published procedures [21]. The purity of the complexes was checked by ^1H and ^{31}P NMR; it was 98–99%.

The chromatographic analysis of reaction mixtures was performed with a Chrom-5 device (1.0-m column; stationary phase 5% SE-30 on Inerton N-Super 0.16–0.20 mm; carrier gas He; flame ionization detector; column heating from 50 to 170°C at a rate of 100 deg min^{-1} followed by keeping at 170°C for 4 min; vaporizer temperature 270°C; hydrogen flow rate 30 ml min^{-1}; internal reference *n*-tetradecane).

The GC–MS analysis was performed on a TurboMass-Gold device (30 000 × 0.32-mm capillary colunm coated with XLB-5; carrier gas He, flow rate 1.2 ml min^{-1}; detection by total ion current; column heating from 50 to 280°C at a rate of 7.5 deg min^{-1} followed by keeping at 280°C for 2 min; internal reference *n*-tetradecane).

The NMR spectra were recorded on a Varian Unity-300 spectrometer at 25°C. Working frequency: 300 MHz for ^1H and 121 MHz for ^{31}P. The ^1H chemical shifts were determined relative to residual protons of $CDCl_3$, and the ^{31}P shifts, relative to external 85% H_3PO_4.

Standard procedure of kinetic experiments. To 3–6 mg of a Pt(II) complex we added 0.3–0.9 ml of a mixture of CCl_4, alkene, and CH_3CN (cosolvent), 1 : 1 : 1 by volume (25°C). The mixture was degassed and evacuated to 300 Pa. Then it was heated at 120°C, and the concentration of the addition product was determined by GLC with *n*-tetradecane as internal reference.

To check the stability of the catalyst, 40-mg portions of *cis*-$PtCl_2(PPh_3)_2$ were placed in three ampules, and one of the following mixtures was added: 4 ml of CH_3CN + 4 ml of CCl_4 + 4 ml of 1-hexene; 4 ml of CCl_4 + 4 ml of CH_3CN; 4 ml of 1-hexene + 4 ml of 1-hexene + 4 ml of benzene. The mixtures were degassed and sealed in a vacuum. The ampules were heated at 120°C for 10.5 h. The solutions were evaporated to dryness in a vacuum, and the residue was washed with hexane. The isolated substances were analyzed by IR and ^{31}P NMR spectroscopy (solvent $CDCl_3$).

The constants of the product formed by addition of tetrachloromethane to 1-hexene were published previously [4, 7].

ACKNOWLEDGMENTS

The study was performed within the framework of the Joint Program of CRDF and Ministry of Education of the Russian Federation “Basic Research and Higher Education” (grant no. REC 007).

The authors are sincerely grateful to R.A. Cherkasov for useful advices given during discussion of this paper.

REFERENCES

1. Kharasch, M.S., Jensen, E.V., and Urry, W.H., *J. Am. Chem. Soc.*, 1947, vol. 69, no. 5, p. 1100.
2. Tarkhanova, I.G., Smirnov, V.V., and Rostovshchikova, T.N., *Kinet. Katal.*, 2001, vol. 42, no. 2, p. 216.
3. Kotora, M., Adamek, F., and Hajek, M., *Catal. Lett.*, 1993, vol. 18, no. 4, p. 345.
4. Grigg, R., Delvin, J., Ramasubbu, A., Scott, R.M.,

and Stevenson, P., *J. Chem. Soc., Perkin Trans. 1*, 1987, no. 7, p. 1515.

5. Freidlina, R.Kh., Velichko, F.K., and Terent'ev, A.B., *Usp. Khim.*, 1984, vol. 53, no. 3, p. 370.
6. Suzuki, T. and Tsuji, J., *J. Org. Chem.*, 1970, vol. 35, no. 9, p. 2982.
7. Zazybin, A.G., Khusnutdinova, Yu.R., and Solomonov, B.N., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 3, p. 515.
8. Gasanov, R.G., Dolgushin, A.I., Yanovskii, A.I., Klemenkova, Z.S., Lokshin, B.V., Petrovskii, P.V., and Rybinskaya, M.I., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1997, no. 6, p. 1174.
9. Brune, H.A., *Chem. Ber.*, 1984, vol. 117, no. 9, p. 2791.
10. Borisoglebskii, S.V., Vedernikov, A.N., Zazybin, A.G., and Solomonov, B.N., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 12, p. 1977.
11. Bland, W.J., Davis, R., and Durrant, J.L.A., *J. Organomet. Chem.*, 1985, vol. 280, no. 3, p. 397.
12. Simal, F., Wlodarczak, L., Demonceau, A., and Noels, A.F., *Tetrahedron Lett.*, 2000, vol. 41, no. 32, p. 6071.
13. Grigg, R., Stevenson, P., and Worakun, T., *J. Chem. Soc., Chem. Commun.*, 1985, no. 14, p. 971.
14. Tsuji, J., Sato, K., and Nagashima, H., *Tetrahedron*, 1985, vol. 81, no. 2, p. 393.
15. Dneprovskii, A.S., Ermoshkin, A.A., Kasatochkin, A.N., and Boyarskii, V.P., *Zh. Org. Khim.*, 2003, vol. 39, no. 7, p. 994.
16. Asscher, M. and Vofsi, D., *J. Chem. Soc.*, 1963, no. 3, p. 1887.
17. Vedernikov, A.N., Sayakhov, M.D., Zazybin, A.G., and Solomonov, B.N., *Zh. Org. Khim.*, 1998, vol. 34, no. 6, p. 862.
18. Appel, R., Knoll, F., Michel, W., Morbach, W., Wihler, H.-D., and Veltmann, H., *Chem. Ber.*, 1976, vol. 109, p. 58.
19. Fischer, H., *Chem. Rev.*, 2001, vol. 101, no. 12, p. 3581.
20. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
21. Brauer, G., *Handbuch der präparativen anorganischen Chemie*, Stuttgart: Ferdinand Enke, 1954.