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Reactions of vanadocene with aliphatic halides

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Abstract

Primary, secondary and tertiary aliphatic halides have been shown to react with vanadocene by oxidative addition to give (alkyl)(halogeno)vanadocenes. The primary product is stable if the alkyl group is methyl, but olefin and alkane are formed in the case of alkyl groups having hydrogen atoms on an sp^3 carbon β to the halogen. In the reaction of vanadocene with isopropyl and t-butyl bromide a significant amount of molecular hydrogen is produced, and the percentage of alkane falls almost to zero in the case of t-butyl bromide. ESR evidence is presented for some of the V^{IV} intermediates.

Introduction

At least two mechanisms can be distinguished for the initial interaction of a low valent metal compound and an organic halide [1]. One of these involves a dissociative-electron-capture process in which an electron is transferred from the metal to the organic halide to give a free radical and a metal halide. The radicals can react with a second metal ion to yield a σ-alkyl metal complex or may undergo typical radical reactions. This type of mechanism has been established for chromium(II) and cobalt(II) salts [1]. It involves a change of the formal oxidation state of the metal ion by one. The second process involves an oxidative addition of the organic halide to a metal complex, with a change of the oxidation state by two units. Both primary reactions may lead to dimers of the organic residues of the halides. Various mechanisms have been considered for this process; free radicals may be involved, or dialkyl metal complexes which undergo reductive elimination.

We describe here the results of a study of the behaviour of vanadocene in these reactions. Vanadocene seemed to be particularly suited for such a study since it has been reported to react with allyl and benzyl halides as well as with primary, secondary and tertiary aliphatic halides [2]. Furthermore it has been established that C–C coupling occurs in the reaction with benzylic halides [2,3], and it was assumed by analogy that this is also the case for aliphatic halides [2].

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Results

Ethyl bromide and vanadocene

A suspension of vanadocene in diethyl ether was allowed to react for 48 h with a three-fold excess of ethyl bromide. The initially green-blue suspension turned dark blue, and a blue solid, identified upon isolation as bromo vanadocene, was obtained in 89% yield. Experiments carried out on a high-vacuum line connected to a Töpler pump permitted quantitative analyses of the organic products (Table 1). The composition of the gas was determined by GLC. Diphenylmethane and benzene were used as solvents, and the reaction in diphenylmethane found to be slower. The solutions in diphenylmethane became blue-green, but those in benzene dark-blue.

The only gaseous products identified were ethane and ethene, which were formed in a ratio of 1.7/1 irrespective of the solvent and the temperature used. No butane, the product of dimerization, was detected. The composition of the gas rules out reaction via free ethyl radicals, for in that case the ratio of dimers to disproportionation products should be different [4]. It seems probable that the olefin is the result of a β-hydrogen elimination from a σ-organometallic complex, with ethane then resulting formally from a combination of a metal hydride in the elimination of ethene with an ethyl group of a σ-alkyl metal complex. For this equimolar amounts of ethane/ethene would be expected, but the excess of ethane may be the result of partial polymerization of ethene. Indeed, estimation of the total yield on the basis of ethane gives a product balance of 100%

Isopropyl bromide and vanadocene

The reaction of this halide with an equimolar amount of vanadocene in diphenylmethane was much faster than that with ethyl bromide (Table 2). In addition to propane and propene, in the constant ratio of 1/3, molecular hydrogen was formed in the amount given in Table 2. No dimers were formed, and so a radical process for product formation can again be excluded.

t-Butyl bromide and vanadocene

Vanadocene reacted very rapidly with an equimolar amount of t-butyl bromide in tetrahydrofuran at room temperature. The solution turned black-blue immediately after mixing, and after 30 s a vigorous gas evolution was observed. After 1 min the solution was dark-blue. GLC analysis of the gaseous phase showed isobutane and isobutene to be present in a ratio of 1/24. GLC analysis of the solution revealed the

Table 1

Reactions of ethyl bromide with vanadocene

Cp_2V (mmol)	EtBr (mmol)	Solvent [a]	*t* (h)	*T* (°C)	Yield of gaseous products [b] (%)
0.87	0.85	Ph_2CH_2	48	25	58.2
0.89	0.89	Ph_2CH_2	48	30	57.3
1.23	1.18	C_6H_6	48	25	82.5
1.20	1.23	C_6H_6	20	40	84.2
1.54	1.55	C_6H_6	23	60	81.8

[a] 5.0 ml solvent. [b] Calculated on the basis of the minor component.

Table 2

Reactions of isopropyl bromide with vanadocene in diphenylmethane [a] at room temperature

Cp_2V (mmol)	i-PrBr (mmol)	t (h)	H_2 (mmol)	C_3H_8/C_3H_6 (mmol)	Yield of organic gases [b] (%)
1.22	1.18	2	0.25	1.06	89.6
1.26	1.24	2	0.32	1.12	90.3
1.02	1.01	1	0.24	0.88	87.1
0.94	0.90	1	0.22	0.77	85.6

[a] 5 ml solvent. [b] Yield relative to isopropyl bromide.

presence of three additional organic products, each in ca. 1% yield on the basis of the peak area. From GLC-MS data the structures were assigned as t-butylcyclopentadiene, tetramethylbutane, and 2-methyl-4,4-dimethyl-1-pentene. The latter could be formed by the attack of a t-butyl radical on isobutene. Molecular hydrogen was again detected. Table 3 lists the results of the quantitative analysis.

Methyl halides (X = I, Br) and vanadocene

The nature of the products in the above reactions is not consistent with the intermediacy of free radicals, and instead, oxidative addition of the alkyl halides to vanadocene and subsequent β-hydrogen elimination is suggested. The feasibility of oxidative additions of aralkyl halides to vanadocene has been established in the accompanying publication [3], and C–C bond formation attributed to radical coupling [3]. We investigated the possibility of oxidative addition of aliphatic halides to vanadocene by examining the reaction with methyl halides. The product of oxidative addition might be expected to be stable in this case because there are no hydrogen atoms on a sp^3-hybridized carbon atom in a β-position, and indeed, (chloro)(methyl)vanadocene, obtained by treatment of dimethyl vanadocene with hydrochloric acid is a stable compound [5].

A suspension of vanadocene in n-hexane was treated with a slight excess of methyl iodide for 2 h at room temperature. Cooling to −78 °C gave dark-green(iodo)(methyl)vanadocene (70%) m.p. 213 °C. Similarly a slight excess of methyl bromide (at −5 °C) was added to vanadocene in petroleum ether also at −5 °C and the mixture then allowed to warm to room temperature and kept there for 2 h, subsequent cooling to −78 °C gave dark green crystals (81%) of m.p. 191–194 °C. Both compounds show a strong ESR absorption, typical of

Table 3

Reactions of t-butyl bromide with vanadocene in diphenylmethane [a] at room temperature

Cp_2V (mmol)	t-BuBr (mmol)	t (min)	H_2 (mmol)	C_4H_{10}/C_4H_8 (mmol)	Yield of organic gases [b] (%)
1.38	1.38	30	0.43	1.21	87.7
1.30	0.96	30	0.25	0.77	80.2
1.21	1.09	30	0.38	0.92	84.4
0.57	0.54	30	0.17	0.46	85.2
0.61	0.57	30	0.20	0.48	84.2

[a] 5 ml solvent. [b] Yields relative to t-butyl bromide.

vanadium(IV) [6]: (iodo)(methyl)vanadocene, g 1.9951, a a_V 6.33 mT; (bromo)(methyl)vanadocene, g 2.0120, a_V 6.62 mT. This information together with elemental analyses, establishes the identities of the new compounds.

Reaction of benzylvanadocene with methyl iodide or t-butyl bromide

In our study of the reaction of benzyl bromide with vanadocene [3] we showed that benzylvanadocene reacts with benzyl bromide to generate free benzyl radicals, which are responsible for the formation of bibenzyl. In order to find out whether alkylvanadocenes ($RVCp_2$) are intermediates in the reaction sequence leading to products in the case of aliphatic halides, we treated benzyl vanadocene with methyl iodide and with t-butyl bromide, but even after several days in each case no conversion of the halide could be detected by GLC. In the above-mentioned reaction of benzyl bromide with vanadocene, in contrast, it was demonstrated that both benzylvanadocene and methylvanadocene react with benzyl bromide.

ESR-spectroscopic measurements

From the above results vanadium(IV) compounds seemed to be the initial intermediates in the reaction of alkyl halides with vanadocene. These were stable in the case of methyl halides, and their participation in the reactions of ethyl bromide, isopropyl bromide, and t-butyl bromide was deduced indirectly from the product composition.

In a flow ESR experiment we tried to identify a vanadium(IV) species in the interaction of vanadocene with alkyl halides, as we did successfully for the reaction with benzyl bromide [3]. With ethyl bromide and isopropyl bromide this approach was unsuccessful, the reactions being too slow for build-up of a sufficiently high concentration of a vanadium(IV) species for detection by ESR spectroscopy. In the case of t-butyl bromide, however, ESR signals were observed. When THF solutions of vanadocene and t-butyl bromide were mixed in a flat cell in the cavity of the ESR spectrometer at −30 °C no signal was observed, but at −21 °C an eight-line spectrum (Fig. 1) with 1.9954 and a_V 4.61 mT was recorded. A careful search between −20 and −30 °C revealed fragments of another eight-line signal with g 2.00 and a_V ca. 6.1 mT. These lines disappear on heating to −20 °C, and the other

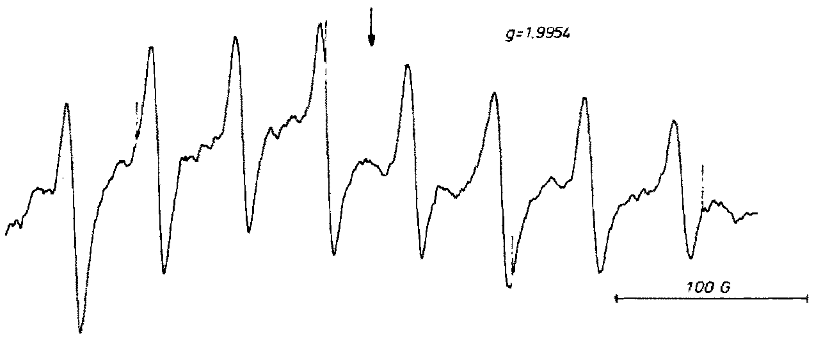


Fig. 1. ESR spectrum, obtained at −21 °C after rapid mixing of THF solutions of vanadocene and t-butyl bromide.

signal also breaks down above −19 °C. The temperature range in which spectra can be observed is rather small, indicating the transient nature of the species concerned.

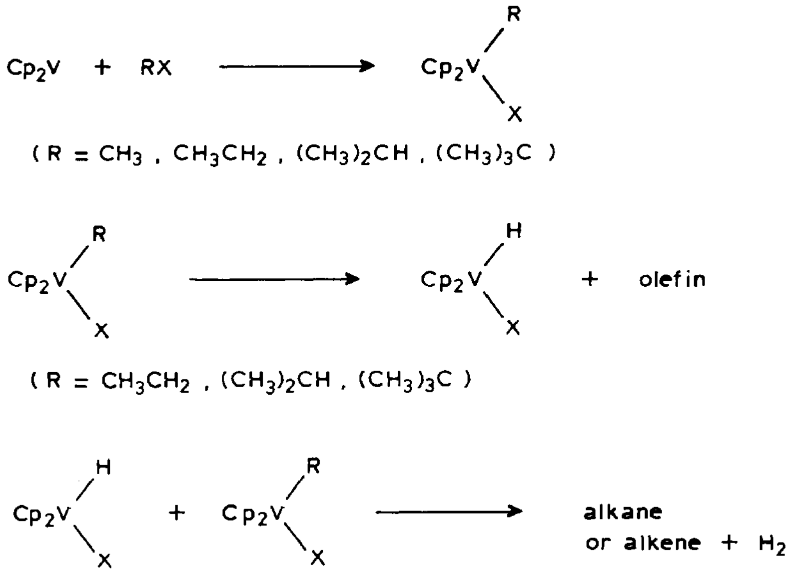
The signal with g 2.00 and a_V 6.1 mT can be assumed to come from the primary product of oxidative addition of t-butyl bromide to vanadocene. The coupling parameter agrees well with those for other species of this type [6]. The coupling constant a_V 4.61 mT is assigned to (bromo)(hydrido)vanadocene, formed by elimination of isobutene from the primary product. There is an analogy for this in the literature, in that the reaction of triethyltin hydride with vanadocene gives hydrido triethyltinvanadocene with a_V 4.16 mT [7], though in that case a coupling of 1.46 mT with the hydrogen atom was found. In our case the hydrido complex might have a slightly different structure that places the hydrogen atom in the nodal plane of the orbital carrying the unpaired electron, so that there might be negligible interaction of the hydrogen nucleus with the unpaired electron. It is evident, however, that in the t-butyl bromide reaction vanadium(IV) compounds are intermediates.

Discussion of the results

Primary, secondary, and tertiary alkyl halides and aralkyl halides evidently undergo oxidative addition to vanadocene as initial step. The primary product is stable when the alkyl group is methyl. In the case of benzyl a subsequent rapid dissociation into halogenovanadocene and benzyl radicals takes place [3]. From this we deduce that a vanadium–carbon bond is rather weak and can undergo homolytical cleavage even at room temperture if a stabilized radical can be formed. Alkyl groups having a hydrogen atom in β-position to the halogen atom give rise to different behaviour, β-hydrogen elimination becoming more pronounced the more hydrogen atoms are available. This process turns out to be the most favorable one energetically, and olefins and alkanes are formed. The proportion of olefin increases rapidly on going from the ethyl bromide to t-butyl bromide. The reactions of isopropyl bromide and t-butyl bromide give appreciable amounts of molecular hydrogen, and it appears that olefin elimination generates an unstable hydrido intermediate from which either molecular hydrogen, is formed, or by a reaction with the primary product of oxidative addition, alkane. Alkane is the major product when the alkyl group is ethyl, but almost absent when it is t-butyl.

Alkane and hydrogen cannot be formed in a unimolecular process. There is no evidence that these reactions involve generation of a vanadium complex that carries either one hydrogen atom and one alkyl group or two hydrogen atoms. It is possible that binuclear complexes may be intermediates, and further investigations of this question are needed.

An important conclusion is that free radicals are not involved in the product-forming steps. In no case is the ratio of alkene/alkane that expected for a free radical process [4]. In all cases dimers would have been formed (in differing but significant amounts). Also molecular hydrogen cannot be the result of hydrogen atom recombination. If the reactions of ethyl bromide, isopropoyl bromide, or t-butyl bromide with vanadocene are carried out in toluene as solvent, any radicals formed would be expected to abstract hydrogen atoms from the solvent, and this should give rise to products derived from the latter; in particular bibenzyl, since this did not occur, the presence of free radicals can be safely excluded in all cases.



Scheme 1

Vanadocene does not react with alkyl- and aralkyl halides by a dissociative electron capture mechanism. The question remains open as to which properties of an organometallic compound determine its mode of reaction. i.e. either dissociative electron capture or oxidative addition. The reduction potential alone cannot be decisive; it could not explain, for example, why vanadocene, $E_{1/2}$ -0.55 V [8], undergoes oxidative addition to aliphatic halides whereas chromium(II) chloride · *n* (THF), $E_{1/2}$ -0.62 V in acetonitrile [9], does not [1]. Furthermore, whereas chromium(II) chloride reacts by dissociative electron capture with benzyl halides [10], vanadocene undergoes oxidative addition.

In Scheme 1 we show the mechanism of reaction of vanadocene with alkyl halides in so far as our investigations have led to definite conclusions.

The reported assumption [2] that the reaction of vanadocene with aliphatic alkyl halides gives dimers in high yield is incorrect, the vanadocene behaving like other transition metal complexes. C–C coupling reaction involving σ-alkyltransition metal complexes in which the alkyl groups carry hydrogen atoms in the β-position remain exceptional.

Experimental

For details of analytical instruments, solvents, reaction conditions, and preparation of vanadocene see ref. 3.

(Iodo)(methyl)vanadocene

A stirred solution of 0.79 g (4.35 mmol) of vanadocene in 20 ml n-hexane was treated with 0.3 ml (0.68 g ≡ 4.82 mmol) of methyl iodide. After 2 h at room temperature the suspension was cooled to $-78\,^{\circ}$C to complete the crystallization. The blue-green crystals (0.98 g ≡ 70%) were isolated by filtration, m.p. 213°C. Analyses. Found; C, 40.57; H, 3.52; I, 39.21. $C_{11}H_{13}VI$ (323.1) calc: C, 40.90; H, 4.05; I, 39.28%.

(Bromo)(methyl)vanadocene

A suspension of 0.74 g (4.08 mmol) of vanadocene in 25 ml of petroleum ether was cooled to −30 °C and 0.23 ml (ca. 0.39 g ≡ 4.16 mmol) of methyl bromide (cooled to −5 °C) was added. The flask was sealed and the mixture warmed with stirring to room temperature. After 2 h at room temperature the vessel was cooled to −78 °C, and the product (0.91 g ≡ 81%) isolated as dark-green crystals. mp. 191–194 °C. Analyses. Found: C, 47.62; H, 4.46; Br, 29.31. $C_{11}H_{13}V$ Br (276.1) calc: C, 47.86; H, 4.75; Br, 28.95%.

Vanadocene and ethyl bromide

Vanadocene (6.60 g, 14.4 mmol) was added to 70 ml of diethyl ether (in which it did not all dissolve) and 4.38 g (40.2 mmol) of ethyl bromide were added slowly at room temperature. The mixture first become dark green, then dark blue, and dark blue crystals separated. After 48 h the suspension was cooled to −78 °C, and the precipitate was isolated, washed with n-hexane, dried under vacuum (1.3 Pa) and shown to be bromovanadocene (3.33 g, 89%) identical with an authentic sample.

Vanadocene and t-butyl bromide

A suspension of vanadocene (1.88 g, 10.4 mmol) in 80 ml of n-hexane was treated with 1.55 g (11.3 mmol) of t-butyl bromide with stirring. A vigorous gas evolution took place immediately, the solution turned blue, and a blue solid separated. Partial removal of the solvent (40 ml) and cooling to −78 °C gave 2.52 g (92%) of bromovanadocene.

Identification of molecular hydrogen in the reaction of vanadocene with t-butyl bromide

Molecular hydrogen was identified indirectly by catalytic hydrogenation of iso-butene. The vessel in which the reaction of vanadocene with t-butyl bromide was performed was connected by a tube to a second vessel containing Pd on charcoal in diphenylmethane. After 8 h the gas phase was analysed by GLC, and it was found that the ratio of isobutene to butane, which is 24/1 under normal conditions, had changed to 1/16.

Reactions of ethyl bromide, isopropyl bromide, and t-butyl bromide with vanadocene in toluene

Solutions containing ca. 1 mmol vanadocene and equimolar amounts of the halide in 4.0 ml toluene were kept at room temperature for 48 h (ethyl bromide), 1 h (isopropyl and t-butyl bromide). GLC analysis with cumene as internal standard on a SE 30 10% glass column (6 m × 1/4 cm) showed that no products derived from benzyl radicals (bibenzyl or coupling products of benzyl with alkyl groups) had been formed.

Analysis of the gaseous products in the reactions of vanadocene with alkyl halides

The reactions were carried out on a high-vacuum line connected with a Töpler pump. The gas was analyzed by GLC (on a 50 cm fused silica Al_2O_3), glass capillary column. The amount of hydrogen was evaluated by allowing the gases to expand through two cold traps (77 K) and measuring the volume of the gas which passed through. The organic gases were then regenerated by heating the cold traps to −40 °C and their proportions determined by GLC.

Details of the reaction conditions are given in Tables 1–3.

ESR measurements

The flow ESR experiments were carried out as described in ref. 3.

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