Journal of Fluorine Chemistry, 64 (1993) 101–105

Ligand effect on regioselectivity in the addition reaction of tetrachloromethane with trifluoroethene catalyzed by copper(I) complexes

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(Received July 14, 1992; accepted November 8, 1992)

Abstract

The regioselectivity of the addition reaction of tetrachloromethane with trifluoroethene is influenced by the structure of the amine ligand in the copper(I) complex used as the catalyst. The regio isomer ratio varied over the range 0.86–2.72 indicating a significant ligand effect on the regioselectivity. The results confirm the assumption that the addition reaction proceeds in the coordination sphere of the copper complex.

Introduction

The regioselectivity of radical addition reactions is not yet well understood. Several directing effects are apparently in competition and the final orientation of radicals to the carbon–carbon double bond is difficult to predict. After extensive work involving more than 20 years of experimental effort, the following directing effects controlling the orientation of radical addition have been reported: bond strengths, polar and steric effects [1]. All these effects compete in a rather complex manner and it is thus not surprising that a simple rule cannot be formulated [2–5]. Generally, the addition of free radicals to unsymmetrical alkenes proceeds with high regioselectivity when a considerable difference exists in the bulkiness of the substituents at the vinylic carbons. Because almost all substituents are significantly bulkier than hydrogen atoms, in most cases addition proceeds preferentially at the less-substituted carbon with more than 99% regioselectivity. An exception is fluorine, which is not a sterically demanding substituent. Its small van der Waals' radius (1.35 Å) closely resembles hydrogen (1.2 Å). Hence, fluoroethenes have been found to be very suitable model alkenes for regioselectivity studies. To date, all regioselectivity studies of addition reactions have been performed in the gas phase, mostly under photochemical conditions [1–5].

Recently, we have studied the addition reactions of haloalkanes with alkenes in the liquid phase in the presence of transition metal complexes

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0022-1139/93/$6.00

as catalysts leading to >99% regioselectivity. The results obtained indicate that, in contrast to classical initiation, catalytic addition is not a free-radical chain process and radicals, presumably coordinated to the central metal atom, react with carbon–carbon double bonds via an inner sphere path [6, 7]. In a previous paper, we described the effect of the catalyst on the regioselectivity of the addition of tetrachloromethane to trifluoroethene in the presence of Cu, Ru and Pd catalysts and dibenzoyl peroxide as an initiator [8]. The observed effect of the catalyst on the regioselectivity was explained by the ability of the catalyst to coordinate (Cu) or not to coordinate (Pd) both the trichloromethyl radical and trifluoroethene. The aim of the present study was to examine the effect of ligands on the regioselectivity of addition reactions catalyzed by copper(I)–amine complexes containing various nitrogen ligands.

Results and discussion

The addition reaction of tetrachloromethane with trifluoroethene leading to two regio isomers **1** and **2** was chosen as the model reaction [eqn. (1)]:

$$CCl_4 + CHF{=}CF_2 \xrightarrow[80\ °C]{CuL_2Cl} \underset{\mathbf{(1)}}{CCl_3CHFCF_2Cl} + \underset{\mathbf{(2)}}{CHFClCF_2CCl_3} \qquad (1)$$

As expected, preferential formation of isomer **1** was observed, indicating that attack at the less sterically hindered and less electrophilic CHF site by the electrophilic CCl_3 species is favoured. The effect of the structure of primary, secondary and tertiary amines when used as ligands in the copper catalysts (CuL_2Cl) on regioselectivity in the addition reaction is summarized by the results given in Table 1.

No significant differences were observed in the **1**:**2** isomer ratio (as reflected by the rate constants ratio k_1/k_2 for the formation of both isomers and by the percentage attack at the CHF and CF_2 sites) with primary and tertiary amines (2.19–2.51; 69–71:31–29) other than ethylamine (1.70; 63:37). This indicates a weak ligand effect with respect to primary and tertiary amines. However, a more interesting situation has been encountered in the case of secondary amines, where the **1**:**2** isomer ratio varied over a much wider range (0.86–2.72; 46–73:54–27). It is noteworthy that, when diethylamine was the ligand, preferential attack occurred to the more substituted and the less favourable CF_2 site as demonstrated by the reversed value for the **1**:**2** isomer ratio (0.86; 46:54). This change in the orientation of the CCl_3 species caused by the diethylamine ligand is surprising. Nevertheless, this may indicate a strong ligand effect on the regioselectivity.

A similar anomalous regioselectivity has been observed for the gas-phase addition of nucleophilic $CH_3^{\cdot}$ radicals to trifluoroethene [1] and has been explained by a theoretical analysis [11]. However, the ligand effect observed in the liquid-phase catalytic addition reaction is more difficult to elucidate. Little is known as to how the regioselectivity of reactions homogeneously

TABLE 1

Effect of the ligand on the regioselectivity in the addition of tetrachloromethane to trifluoroethene

Ligand	Isomer ratio **1**:**2**	Rate constant ratio k_1/k_2	E_s[a]	Gas-phase basicity[b]
ethylamine	63:37	1.70 ± 0.03	−0.07	213.0
propylamine	69:31	2.19 ± 0.01	−0.36	214.4
2-propylamine	70:30	2.36 ± 0.02	−0.47	215.3
butylamine	71:29	2.48 ± 0.01	−0.39	214.9
2-methylpropylamine	70:30	2.39 ± 0.01	−0.93	215.4
1,1-dimethylethylamine	69:31	2.28 ± 0.02	−1.54	217.3
2,2-dimethylpropylamine	71:29	2.51 ± 0.01	−1.74	216.1
cyclohexylamine	69:31	2.28 ± 0.04	−0.79	217.2
benzylamine	71:29	2.48 ± 0.03	−0.38	–[c]
diethylamine	46:54	0.86 ± 0.03	−0.14	221.2
dipropylamine	63:37	1.70 ± 0.03	−0.72	223.1
di(2-propyl)amine	73:27	2.72 ± 0.05	−0.94	225.0
dibutylamine	65:35	1.90 ± 0.09	−0.78	224.3
pyrrolidine	61:39	1.57 ± 0.02	–[c]	220.4
triethylamine	71:29	2.41 ± 0.11	−0.21	227.7
tripropylamine	69:31	2.30 ± 0.02	−1.08	229.9
tributylamine	71:29	2.47 ± 0.02	−1.17	231.3
trihexylamine	70:30	2.37 ± 0.01	−0.90	–[c]

[a] Taft steric constants [$E_s(CH_3) = 0$] [9].
[b] See ref. 10.
[c] Data not available.

catalyzed by transition metal complexes may be affected by polar and steric effects arising from the ligands (for example, only an empirical rule explaining the regioselectivity of olefin insertion into metal complexes has been proposed [12]). Generally, however, addition reactions proceed preferentially at the least substituted carbon atom of a C–C double bond. Such a rule may be adequate to explain the carbonylation of alkenes in the presence of cobalt complexes [13], where steric effects play an important role in the regioselectivity.

In order to obtain more information, correlation of the **1**:**2** isomer rate constant ratio with the gas-phase basicities of the amine ligands and with the Taft steric constants (E_s) of the alkyl substituents at nitrogen has been attempted. Gas-phase basicities were used because the intrinsic basicities of alkylamines increase regularly with increasing substitution, whereas solvation effects in solution result in anomalies observed [10]. A reasonable correlation with the gas-phase basicity ($R = 0.9604$) and E_s ($R = 0.9399$) has been found with dialkyl-substituted amines. However, the results presented in Table 1 indicate that the ligand effect is more complex and cannot be explained by polar or steric effects arising from the ligand. Nevertheless, the results from the present regioselectivity study confirm our previous assumption that the addition reaction proceeds in the coordination sphere of the metal atom, which is important information from a mechanistic point of view. It is assumed that the attached ligand contributes to the electronic arrangement in the trichloromethyl radical (the term CCl_3 species is therefore used in this paper) and of the alkene via coordination. Similar conclusions were obtained recently for the ligand effect using the Hammett correlation for the addition reaction of substituted styrenes with chloroform [14].

Experimental

GC analyses were performed on a HP-5890A chromatograph with a HP Ultra-1 capillary column. Mass spectra were measured on Schimadzu QP-100 and VG Analytical mass spectrometers.

Materials

Tetrachloromethane (Lachema, Brno) and all amines (Fluka, Buchs) were distilled prior to use. Trifluoroethene was prepared via dehalogenation of 1-bromo-1-chloro-1,2,2-trifluoroethane (kindly provided by Léčiva-Dolní Měcholupy) [8].

Additions catalyzed by CuCl–amine complexes — typical procedure

Trifluoroethene (2.05 g, 25 mmol) was condensed into a 60 ml glass ampoule equipped with a septum and a magnetic stirrer, then tetrachloromethane (50 ml) and finally CuCl (0.1237 g, 1.25 mmol) were added. The ampoule was heated to 80 °C and a portion of the amine (2.50 mmol) was injected through the septum. During the next 8 h another portion of amine (21 mmol) was added continuously to the reaction mixture. The samples from the reaction mixture were washed with 50 ml of 10% HCl, the organic layer separated, dried with anhydrous $CaCl_2$ and subjected to GC and MS analyses. The ratio of isomers **1** and **2** was constant during the course of reaction irrespective of their yields which varied from 4 to 97%. Regio isomers **1** and **2** were identified by MS analysis. Their spectra have been described in a previous paper [8]. The ratio of both isomers was calculated from GC data according to the relationship $k_1/k_2 = x_1/x_2$ (x = degree of conversion). The average value of five analyses was calculated in each experiment. Experiments with secondary amines were carried out in duplicate and gave the same values.

References

1 G. Modena and G. Scorrano, in S. Patai (ed.), *The Chemistry of the Carbon–Halogen Bond*, John Wiley and Sons, New York, 1973, p. 385.
2 J.M. Tedder and J.C. Walton, *Acc. Chem. Res.*, *9* (1976) 183.
3 J.M. Tedder and J.C. Walton, *Adv. Phys. Org. Chem.*, *16* (1978) 51.
4 J.M. Tedder, *Angew. Chem.*, *94* (1982) 433.
5 B. Giese, *Angew. Chem.*, *95* (1983) 771.
6 M. Hájek, P. Šilhavý and B. Špirková, *Collect. Czech. Chem. Commun.*, *55* (1989) 2949.

7 F. Adámek, M. Hájek and Z. Janoušek, *Collect. Czech. Chem. Commun.*, *57* (1992) 1291.
8 M. Kotora and M. Hájek, *J. Fluorine Chem.*, *55* (1992) 57.
9 C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, John Wiley and Sons, New York, 1980, p. 65.
10 D.H. Aue, H.M. Webb and M.T. Bowers, *J. Am. Chem. Soc.*, *98* (1976) 311, 318.
11 E. Canadel, O. Eisenstein, G. Ohanessian and J.M. Poblet, *J. Phys. Chem.*, *89* (1985) 4856.
12 G. Henrici-Olive and S. Olive, *Top. Curr. Chem.*, *67* (1976) 118.
13 G.W. Parshall, *Homogeneous Catalysis*, John Wiley and Sons, New York, 1980, p. 87.
14 M. Hájek and Š. Krupička, in preparation.