

DEHALOGENATION OF CHLOROARENES WITH SODIUM DIHYDRIDOBIS(2-METHOXYETHOXO)ALUMINATE IN THE PRESENCE OF TRANSITION METAL COMPOUNDS

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Dehalogenation of low-chlorinated arenes such as *p*-dichlorobenzene or chlorobenzene with the title hydride is accelerated in the presence of transition metal species formed in situ from the corresponding 2,4-pentanedionates. Their efficiency decreases in the order: $\text{Co} \approx \text{Ni} \approx \text{Pd} > \text{Cu} \gg \text{Mn} > \text{Fe}$ which results from changes of their activity and stability. The dehalogenation is well described by a kinetic model consisting of the set of dehalogenation steps which are first order in the chloroarene combined with the catalyst deactivation which is second order in the transition metal compound.

Group I – III metal hydrides are in general poor agents for dehalogenation of nonactivated low-chlorinated arenes such as chlorobenzene, chloronaphthalene etc. In several cases, however, their efficiency substantially increased upon addition of transition metal salts. Such a promoting effect has been observed in the MgH_2 dechlorination of chlorobenzene with NiCl_2 , $\text{Ni}(\text{PPh}_3)_4$ (ref.¹) and, to the lesser extent, also with other metal chlorides² ($\text{FeCl}_3 > \text{CrCl}_3 > \text{MnCl}_2 > \text{CoCl}_2$, $\text{TiCl}_3 \cdot 3 \text{ THF} \gg \text{VCl}_3$) and in the NaBH_4 dehalogenation of bromo- and chlorobenzenes with $\text{NiCl}_2(\text{PPh}_3)_2$ (ref.³), using the above metal compounds in substoichiometric (catalytic) amounts with respect to both the hydride and the substrate. Although NaH was found to be very poor reagent for the more reactive bromobenzene⁴, the reaction has been readily effected in the presence of Pd(II)-(long chain ether-phosphane) complexes as catalysts⁵.

On the contrary, in dehalogenations with LiAlH_4 , only stoichiometric amounts of transition metal chlorides ($\text{NiCl}_2 > \text{FeCl}_2 \gg \text{CoCl}_2$) promoted chlorobenzene dechlorination⁶. A similar situation has been recently found⁷ also in 4-chlorobiphenyl dechlorination with $\text{NaBH}_2(\text{OCH}_2\text{OCH}_3)_2$ where approximately 1 equivalent of the substrate could be dechlorinated per equivalent of NiCl_2 , demonstrating thus a noncatalytic course of the reaction. When compared to the above hydrides, the behaviour of the aluminum analogue, $\text{NaAlH}_2(\text{OCH}_2\text{OCH}_3)_2$ (SDMA), might be a promising exception, based on the strong accelerating effect achieved⁸ in the dehalogenation of aryl halides in the presence of catalytic amounts of Pd(II)-benzonitrile complexes.

Our continuing interest in chemical destruction of noxious polychlorinated hydrocarbons⁹⁻¹¹ led us recently to the study of kinetics of dehalogenation of a series of chlorobenzenes with SDMA (ref.¹²). The slow dehalogenation rate and incomplete dechlorination of the low chlorinated arenes formed during the multistep dehalogenation process resulted in a serious obstacle against the use of this dehalogenating agent for the above mentioned purpose. However, in view of other convenient properties of SDMA (high solubility in aromatic hydrocarbons, safe manipulation) and of its ability to act as a very efficient activating agent in formation of transition metal hydrogenation catalysts (cf. ref.¹³ and references therein), it seemed to us useful to explore this possibility. The results of our attempt to accelerate dehalogenation of the least reactive chloroarenes (chlorobenzene and 1,4-dichlorobenzene) by transition metal compounds as promoters are reported briefly in the present work.

EXPERIMENTAL

Chemicals

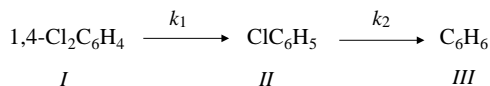
Sodium dihydridobis(2-methoxyethoxy)aluminum, 70% solution in toluene (trade mark Synhydrid, Synthesia Kolin) was used after the actual hydride concentration had been determined iodometrically¹⁴. The solvents (toluene, dioxane, both analytical purity grade) were dried over sodium and redistilled. Chlorobenzene, 1,4-dichlorobenzene (chemical purity grade, Lachema Brno) and metal 2,4-pentanedionates (acac) (Ni(acac)₂, Co(acac)₂, Pd(acac)₂, Co(acac)₃, Cu(acac)₂, Fe(acac)₂, and Mn(acac)₂ – all Fluka chemical purity preparations) were used as obtained. Bis(benzonitrile)palladium(II) dichloride was taken from laboratory stock.

General Dehalogenation Procedure

A thermostatted reaction vessel equipped with a thermometer and a reflux condenser was filled with dry toluene or dioxane (10 ml). Then, 0.5 M toluene solution of 1,4-dichlorobenzene or chlorobenzene (2 ml) were added, followed by the metal pentanedionate dissolved in toluene (3 ml). The magnetically stirred solution was warmed up to the reaction temperature at which SDMA (60% toluene solution) was added in one portion. In all experiments SDMA was taken in threefold molar excess with respect to the chlorine of the chlorobenzene to be dehalogenated. At regular intervals, 0.5 ml samples of the stirred reaction mixture were withdrawn, the unreacted hydride immediately decomposed by aqueous 2 M HCl. After phase separation, the toluene layer was subjected to GLC analysis (Hewlett-Packard 5890 instrument equipped with a capillary glass column (25 m × 0.25 mm) covered by OV-101 silicone elastomer, programmed temperature from 35 °C to 200 °C, calibration by authentic samples, except higher boiling by-products which were calibrated with the use of biphenyl as a standard). The corresponding GC calibration parameters (*A*, *B*) are presented in Table I. The structure of dehalogenation by-products was examined by GC-MS method, using a Varian 3500 capillary gas chromatograph coupled with a Finnigan MAT ITD 800 ion trap mass detector (EI, 70 eV), equipped with a LEO PC 386 SX for data processing with a NIST library of 42 000 spectra (for details of measurement conditions see ref.¹²).

Treatment of Experimental Data

Time-concentration dependences for both the starting chlorobenzenes and their dehalogenated products obtained by GLC analysis were treated in terms of a simple model of stepwise dehalogenation, written for 1,4-dichlorobenzene in the following way:



The analysis showed that the catalyst activity is also time dependent, decreasing steadily during the reaction. This fact was incorporated into the kinetic scheme of dehalogenation which had then the following form:

$$d[\text{cat}]/dt = -k_{\text{deact}} [\text{cat}]^y \quad (1)$$

$$d[I]/dt = -k_1 [I]^x [\text{cat}] \quad (2)$$

$$d[II]/dt = k_1 [I]^x [\text{cat}] - k_2 [II]^x [\text{cat}] \quad (3)$$

$$d[III]/dt = k_2 [II]^x [\text{cat}] \quad (4)$$

where k_{deact} , k_1 , and k_2 are apparent rate constants of the catalyst deactivation and of respective dehalogenation steps depicted in the above reaction sequence (*I* to *II* to *III*), x and y are reaction orders in the catalyst and the substrate. The SDMA concentration, [SDMA], is not written in the rate equations, being considered as constant and included in the respective rate constants (dehalogenations were carried out with the hydride in sufficient excess to justify this assumption). Because of variable properties of the catalyst systems with the metal compound to SDMA molar ratio, the reaction order in SDMA had not been determined and was thus expressed in the rate constant dimension as un-

TABLE I
Characteristics of data treatment

Compound	GLC ^a		R^b , %	k_{error}^c , rel.%	[SDMA] ^d mol l ⁻¹
	A	B			
C ₆ H ₆	1.01	0	—	—	—
ClC ₆ H ₅	1.19	0.024	57	6	0.81
1,4-Cl ₂ C ₆ H ₄	1.82	-0.027	61	5	0.81

^a Parameters of GLC calibration curves, where $[\text{RX}]_{\text{actual}} = (P_{\text{RX}}/(P_{\text{ST}} + P_{\text{RX}})) [A + B (P_{\text{RX}}/(P_{\text{ST}} + P_{\text{RX}}))]$ (weight concentration). ^b R Maximum conversion to which the given dehalogenation was followed and the obtained results treated. ^c The relative error of the rate constant determination. ^d SDMA concentration used in the measurements (SDMA/2 : C₆H_{6-n}Cl_n / n molar ratio was always 3 : 1).

known (i.e. k_1 , k_2 in $[\text{SDMA}]^{-x} \text{ min}^{-1}$, k_{deact} in $[\text{cat}]^{-1} [\text{SDMA}]^{-x} \text{ min}^{-1}$). The set of four differential equations written above was solved numerically according to the Runge–Kutta method with simultaneous optimization of the equation parameters to experimental data with the use of the modified Marquardt method¹⁵. The computations were performed with variable x and y quantities (0, 1, 2) and the fit of the resulting three rate constants to experimental data for the whole course of the reaction was evaluated by comparing the values of the mean standard deviations. Based on these data, the dehalogenation under study is well described for the set $x = 1$, $y = 2$. Maximum conversions (R , %) to which dehalogenation of a given chloro compound was followed and obtained data used in rate constant computation are given in Table I, along with the average relative error in rate constant determination (k_{error} , in rel.%). The rate constants of dechlorination of both chlorobenzenes are listed in Table II.

RESULTS AND DISCUSSION

Our earlier studies (cf. refs^{13,16–18}) on formation of transition metal catalysts by the reaction of metal precursors with SDMA showed that properties of such catalysts depend strongly on a number of reaction parameters (solvent, reaction temperature, the metal to SDMA molar ratio, the sequence of mixing catalyst components, the controlled aging and stabilization, nature of metal precursor etc.), optimization of which is largely empirical. As expected, a similar situation has been observed also in the dehalogenations with analogous metal hydride–transition metal systems (cf. refs^{7,8}).

For that reason we have examined first several different ways of preparation of these dechlorinating agents, and evaluated their efficiency based on the 1,4-dichlorobenzene conversion achieved under identical reaction conditions. To avoid the ill reproducibility of the two phase activations taking place on using insoluble transition metal precursors¹⁸, we have chosen the soluble metal 2,4-pentanedionates. Preliminary experiments with SDMA–Ni(acac)₂ showed that the most convenient treatment is the one step reduction of Ni(acac)₂ with SDMA in the presence of the dehalogenated compound at the temperature of dechlorination reaction. This treatment was thus taken as a general procedure for preparing other SDMA–transition metal dechlorination systems studied (see Experimental).

In order to characterize quantitatively the efficiency of the systems studied, some preliminary experiments concerning kinetics of 1,4-dichlorobenzene dehalogenation were performed, using Ni(acac)₂. Dependence of the initial rate of the dehalogenation on the Ni chelate concentration is presented in Fig. 1. The curves indicate a complex metal action. At first sight they resemble an analogous dependence reported by other authors⁸ for dechlorination of 1-chloronaphthalene with SDMA–PdCl₂(C₆H₅CN)₂ (cf. Fig. 2 in the quoted work). One of possible reasons of such behaviour was thought to be agglomeration of metal species to bulkier metal particles with smaller specific surface⁸ (and thus reduced dehalogenation activity). To obtain further information, we have analyzed both the reported dependence⁸ and the above curves in log–log form. While any statistically significant relation has not been found for the SDMA–Pd dehalogenation system, the rate data for SDMA–Ni give linear correlation with different

TABLE II

Rate data and product composition for dehalogenation of 1,4-dichlorobenzene (*I*) and chlorobenzene (*II*) with SDMA-transition metal dehalogenation agents (for conditions see Experimental)

Entry	Metal compound	[cat] · 10 ^{2,a}	<i>k</i> _{deact} ^b	<i>k</i> ₁ ^b	<i>k</i> ₂ ^b	<i>Y</i> _{RX} ^c %	Products, %		
							<i>II</i>	<i>III</i>	by-product
1,4-Dichlorobenzene									
1	–	–	–	0.0011	0.0014	15	13	2	–
2	PdCl ₂ (C ₆ H ₅ CN) ₂	3.3	4.5	0.95	0.12	51	41	3	7
3	PdCl ₂ + 2 PPh ₃	3.4	1.7	0.76	0.17	67	44	7	16
4	PdCl ₂ + 4 PPh ₃	3.2	0.25	0.24	0.089	58	35	6	16
5	Ni(acac) ₂	0.61	32	3.7	1.4	34	27	2	6
6	Ni(acac) ₂	3.8	5.7	1.6	0.18	65	47	3	14
7	Ni(acac) ₂	8.1	4.8	1.4	0.26	70	54	8	9
8	Ni(acac) ₂ ^d	1.5	23	4.7	~10 ⁻⁴	39	–	–	–
9	Ni(acac) ₂ ^d	2.7	~10 ⁻⁴	0.27	~10 ⁻⁴	49	–	–	–
10	Ni(acac) ₂ ^d	4.1	~10 ⁻⁴	0.12	~10 ⁻⁴	64	–	–	–
11	Co(acac) ₂	3.8	4.9	1.3	0.05	62	46	1	15
12	Co(acac) ₂ ^e	3.5	2.8	1.0	0.04	60	57	1	2
13	Co(acac) ₂ ^f	3.6	9.5	3.5	0.23	78	57	4	17
14	Co(acac) ₃	2.0	7.1	1.4	~10 ⁻⁴	50	44	0	6
15	Cu(acac) ₂	3.4	~10 ⁻⁴	0.15	~10 ⁻⁴	45	44	0	1
16	Mn(acac) ₂	3.6	1.3	0.093	0.04	14	11	1	2
17	Fe(acac) ₃	2.1	3.0	0.11	~10 ⁻⁴	8.9	9	0	1
Chlorobenzene									
18	–	–	–	–	5.9 · 10 ⁻⁴	10	–	–	–
19	Co(acac) ₂	3.0	0.89	–	0.17	29	–	16	13
20	Co(acac) ₂ ^f	2.9	5.7	–	1.9	68	–	53	14

^a Expressed as molar fraction. ^b Eqs (*I*) – (*4*), *k*_{deact} in [cat]⁻¹ [SDMA]^{-x} min⁻¹, *k*₁ and *k*₂ in l^x min⁻¹ mol^{-x}. ^c *Y*_{RX} denotes conversions of *I* and *II* after 3 h reaction. ^d The incremental addition of Ni compound; conversions of *I* after 1 h (entry 8), 2 h (entry 9), and 3 h (entry 10). ^e Dioxane as the solvent. ^f At boiling point of the solvent (110 °C).

slopes for both periods followed (0.41 ($r = 0.975$) for 10 min and 0.31 ($r = 0.972$) for 30 min). The variable fractional order to the metal demonstrates that the catalytic properties of the formed metal species are subject to time changes, which should be incorporated to a kinetic model of the dehalogenation. Treatment of experimental data obtained with Ni(acac)₂ and the other metal pentanedionates studied (for details see Experimental) yielded the best fit for the model involving the set of dehalogenation steps which were first order in the chloro compound, combined with the second order catalyst deactivation. This model (Eqs (1) – (4)) described well the course of the dehalogenation reaction, as demonstrated on dichlorobenzene dehalogenation in Fig. 2 as an example. The corresponding rate constants, along with the product composition at the end of the dehalogenation are collected in Table II.

Prior to discussion of the rate data for individual transition metal systems, the composition of dehalogenation products deserves mentioning. As demonstrated in the Table II, in all the experiments except the noncatalytic dehalogenation, the expected products of hydrogenolytic cleavage (chlorobenzene, benzene) are accompanied by several minor side products. Their total amount is expressed in Table II in mole % determined with the use of biphenyl as the standard (see Experimental). Irrespective of the metal chelate used as a metal precursor in 1,4-dichlorobenzene dechlorination, GC-MS analysis confirmed the presence of 4 responses corresponding to the compounds of the general formula C₁₃H₁₁Cl. Comparison of their mass spectra with those recorded in the instrument library suggested the four possible types which could not be further differentiated. These were: *x*-methyl-*x'*-chlorobiphenyl (IV) and (*x*-chlorophenyl)-phenylmethane (V) isomers, diphenylchloromethane (VI) or *x*-(chloromethyl)biphenyl (VII) isomers.



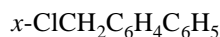
IV



V



VI



VII

The products had relative elution volumes (with respect to toluene) within 3.10 – 3.38, their relative distribution being 5, 30, 35, and 30 per cent. In spite of the already stressed structural uncertainty, these products all would arise from homolytic cleavage of the aryl–Cl bond of the chloroarene followed by interaction of the radicals formed (ClC₆H₅• for IV and V, and Cl• for VI and VII) with the solvent. This cleavage is surely mediated by the transition metal, as similar products have not been found in the SDMA

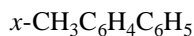
dehalogenations of chlorobenzenes without addition of transition metal compounds in both the previous¹² and this work. Participation of the aromatic solvent in side products formation seems to be confirmed by the strong suppression of this process on using dioxane as the solvent (compare entries 13 and 14, Table II). The complete absence of these products could not be expected, as also here the hydride was used as its toluene solution.

Similarly, GLC analysis of the products of chlorobenzene dechlorination with some SDMA-transition metals yielded two responses corresponding to the compounds of the general formula $C_{13}H_{12}$, suggesting formation of diphenylmethane (VIII) or methylbiphenyl isomers (IX), based on their mass spectra. Their relative elution volumes were 2.85 and 2.94 with respect to toluene, with the relative distribution 65 and 35 per cent.

The rate data in Table II show that the overall effect of transition metal species formed in SDMA-metal precursor systems on the course of the dehalogenation results



VIII



IX

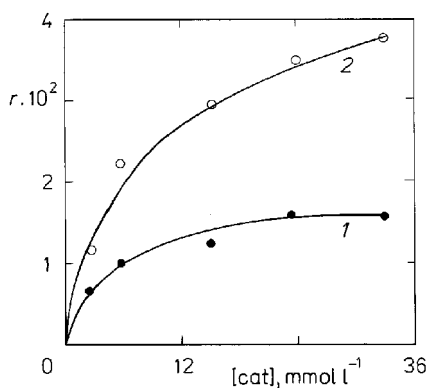


FIG. 1

Dependence of the rate of dechlorination, r ($\text{mol l}^{-1} \text{min}^{-1}$), of 1,4-dichlorobenzene with SDMA-Ni(acac)₂ on Ni(acac)₂ concentration, [cat] (mmol l^{-1}). (For reaction conditions see General Procedure in Experimental.) 1 For 30 min period, 2 for 10 min period

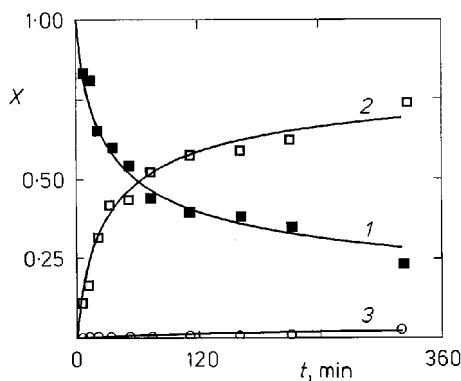


FIG. 2

Comparison of experimental (points) and computed data (curves) for SDMA dechlorination of 1,4-dichlorobenzene (1) to chlorobenzene (2) and benzene (3) (in dioxane, 70 °C, Co(acac)₂ - entry 12 in Table II, X stands for molar fraction). Mean standard deviations of experimental points are 0.033 X (1), 0.027 X (2), and 0.008 X (3)

from both activity and stability of this species. Provided that the model proposed is not formal, then deactivation processes take increasing relative importance due to the higher power function with respect to metal precursor concentration (Eq. (1)). This can be documented, for example, on the results obtained with $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ (entry 2) and those aimed at stabilizing palladium species by addition of PPh_3 during its formation (entries 3 and 4). They reveal that the increased conversion of 1,4-dichlorobenzene achieved with the $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2 + 2 \text{PPh}_3$ system (67% vs 47%) results from the significant suppression of catalyst deactivation (k_{deact} almost 3 times lower in the latter case) while the overall dehalogenation activity remains practically the same (cf. compensation of k_1 and k_2 changes). Further addition of PPh_3 changes both parameters analogously, resulting thus in the decrease of its efficiency (entry 4).

Several experiments aimed at evaluating the role of reaction conditions showed that at least for the nonstabilized metal system $(\text{Ni}(\text{acac})_2)$, entries 5 – 7), the higher activity of the system prepared with the metal precursor in the lower concentration (entry 5) is outweighed by its low stability (cf. k_{deact} 31.5 in entry 1 with e.g. 4.8 in entry 7). As expected, the rate of deactivation increases with increasing temperature (cf. entries 11 and 13), and seems to depend on the solvent (cf. entries 11 and 12). In this connection it is worth mentioning that in the recent study of dehalogenation of chlorobiphenyls with $\text{NaBH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{-NiCl}_2$ (ref.⁷), the higher yields were obtained by portionwise addition of NiCl_2 during the reaction. However, the already discussed high k_{deact} found for the metal species formed at lower metal precursor concentrations (compare entries 5 and 7), which would be the case of incremental addition, speaks against the applicability of this method in our case. The results obtained in such an experiment using $\text{Ni}(\text{acac})_2$ (entries 8 – 10) did confirm this conclusion. Although the analysis of the above data allowed us to specify the role of different reaction parameters, it has not contributed much to the deeper understanding of this process. This question is under further investigation.

In conclusion, the efficiency of the metal chelates studied deserves mentioning. The 1,4-dichlorobenzene conversions obtained under identical reaction conditions could reasonably be taken for comparison. They demonstrate that except Mn and Fe chelates, the other metal compounds give systems that speed up the dehalogenation reaction. Their catalytic effect decreases in the order: $\text{Co} \approx \text{Ni} \approx \text{Pd} > \text{Cu} \gg \text{Mn} > \text{Fe}$. The last entry in Table II illustrates the efficiency of the systems examined in the chlorobenzene dehalogenation. The use of SDMA–transition metal systems to effect dehalogenation of PCB congeners will be reported in a subsequent work.

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