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Mechanism of Dehydrochlorination of 2,2-Diaryl-1,1,1-trichloroethanes with Nitrite and Halide Anions

V. N. Kazin*, M. B. Kuzhin, S. G. Sibrikov, A. V. Sirik, E. A. Guzov, and V. V. Plakhtinskii

Demidov Yaroslavl State University, ul. Sovetskaya 14, Yaroslavl, 150003 Russia
**e-mail: kaz@bio.uniyar.ac.ru*

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Abstract—The reactivity of 2,2-diphenyl-1,1,1-trichloroethane toward halide ions in dipolar aprotic solvents has been studied, and the mechanisms of its reactions with nitrite and halide ions have been compared. The results of kinetic and DFT quantum chemical studies suggest a common bimolecular elimination mechanism for both dehydrochlorination reactions.

Keywords: 2,2-diaryl-1,1,1-trichloroethanes, nitrite and halide ions, dehydrochlorination, kinetics, DFT calculations

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Diaryl-1,1,1-trichloroethanes and their derivatives are intermediate products in the manufacture of various dyes and pigments, dietary supplements, polyfunctional organic reagents, and monomers. Polymers containing trichloroethane fragments possess such important properties as incombustibility and self-extinction, but their thermal stability is not high. Enhanced heat resistance is favored by the transformation of trichloroethane group to dichloroethene or carbonyl.

The set of available dehydrochlorinating agents is fairly large; it includes anhydrous metal alkoxides, solid alkalies and their solutions in water or organic solvents, and organic bases such as pyridine and aromatic and aliphatic amines. We previously reviewed [1] mechanisms of dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes and the effects of substrate structure and reagent and solvent nature on this process. Despite vast chemical information on functionalization and functional transformations of 2,2-diaryl-1,1,1-trichloroethanes, only a few data are available on the reactivity of these compounds toward alkali halides and nitrites. In particular, dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes by the action of alkalies and inorganic salts in various solvents was studied, and optimal reaction conditions were found [2]. It was shown that alkali metal fluorides and nitrites are the most efficient dehydrochlorinating agents for 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DMF, 363 K, substrate-to-reagent ratio 1 : 3). Alkali metal bromides and iodides are less active, and chlorides occupy an intermediate poisition.

Reagent	KNO_2	KF	KCl	KBr	KI
Time, h	0.5–1	0.1–0.3	2.5–3.0	3–3.5	4–4.5
Yield, %	95–97	96–98	94–96	93–95	92–94

The kinetics of dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes with nitrite ions were studied in [3], and an E2 mechanism was proposed on the basis of the experimental data and results of quantum chemical simulation. However, there are no published data on the kinetics and mechanism of dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes with halide ions in dipolar aprotic solvents.

The goal of the present work was to analyze how the reagent nature affects the reactivity and mechanism of dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes. The kinetic studies were performed using 1,1,1-trichloro-2,2-diphenylethane as model substrate and potassium chloride as dehydrochlorinating agent. The effect of the substrate concentration [S] on the reaction rate was studied in DMF at 363 K with excess reagent, i.e., under pseudofirst-order reaction conditions. Table 1 contains the rate constants for the reactions of 1,1,1-trichloro-2,2-diphenylethane with potas-

Table 1. Rate constants of the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane with potassium chloride and nitrite (363 K, DMF, [reagent] = 0.6 M)

Initial substrate concentration $[S]_0$, M	KCl		KNO_2	
	$k_{ef} \times 10^5$, s^{-1} (with respect to the substrate)	$k_{ef} \times 10^5$, s^{-1} (with respect to the product)	$k_{ef} \times 10^4$, s^{-1} (with respect to the substrate)	$k_{ef} \times 10^4$, s^{-1} (with respect to the product)
0.03	7.50±0.33	7.12±0.35	6.35±0.34	6.55±0.31
0.04	7.13±0.31	7.26±0.33	6.26±0.35	6.27±0.29
0.05	7.39±0.35	7.27±0.34	6.27±0.33	6.33±0.34
0.06	7.19±0.34	7.04±0.35	6.11±0.32	6.14±0.34

sium chloride and nitrite. Similarity of the rate constants calculated from the substrate consumption and product formation, as well as material balance data, indicated no accumulation of intermediate or byproducts in the reactions with both potassium chloride and potassium nitrite. It was also found that the rate constant for the reaction with potassium chloride is lower by an order of magnitude than the rate constant for the reaction with potassium nitrite.

The thermodynamic parameters of the dehydrochlorination reactions were derived from the temperature dependences of the rate constants (Table 2). The high negative entropies of activation for the reactions with both chloride and nitrite ions suggest higher ordering of the transition state compared to the initial system, which is typical of bimolecular processes.

We also examined the effect of solvent nature (DMF, *N*,*N*-dimethylacetamide, DMSO, ethanol) on the reaction kinetics. No dehydrochlorination was observed in ethanol. It was interesting to carry out the reaction in a binary mixture of aprotic and protic solvents, DMF–EtOH, at volume ratios of 80 : 20 and 60 : 40. As a result, a correlation was found between log k_{ef} and Dimroth solvatochromic parameter E_T:

$$\log k_{ef} = (4.78 \pm 1.47) - (0.048 \pm 0.01)E_T;$$

$$r = 0.963,\ s = 0.096,\ N = 5.$$

As the E_T value increases, the reaction slows down, and addition of protic solvent sharply reduces the rate constant. The negative coefficient at the Dimroth parameter in the above correlation indicates that the transition state is less polar than the initial system and that no charge appears or disappears in the transition state [4]. Analogous trend was also observed for the reaction with nitrite ion [3].

Table 2. Rate constants and thermodynamic parameters for the reactions of 1,1,1-trichloro-2,2-diphenylethane with potassium chloride and nitrite (DMF, [reagent] = 0.3 M)[a]

KCl		KNO_2	
T, K	$k_{ef} \times 10^4$, s^{-1}	*T*, K	$k_{ef} \times 10^4$, s^{-1}
353	0.32 ± 0.01	333	0.49 ± 0.01
363	0.75 ± 0.03	343	1.52 ± 0.07
383	2.85 ± 0.14	353	4.28 ± 0.24
403	12.59 ± 1.43	363	6.35 ± 0.34
423	33.98 ± 2.62	373	11.62 ± 0.78
E_a 83.34±1.04 kJ/mol $\Delta H^{\neq}$ = 80.18±1.14 kJ/mol log *A* = 18.09±1.45 $\Delta S^{\neq}$ = –104.66±4.25 J mol^{-1} K^{-1}		E_a 80.60±0.62 kJ/mol $\Delta H^{\neq}$ = 77.68±0.73 kJ/mol log *A* = 19.39±1.49 $\Delta S^{\neq}$ = –93.20±4.53 J mol^{-1} K^{-1}	

[a] The entropy of activation was calculated for 363 K.

The effect of halide ion nature on the kinetics of dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane in DMF at 363 K ($[S]_0$ = 0.03 M, $[Hlg]_0$ = 0.3 M). We failed to measure the rate constant for the reaction with KF at 363 K because of its very high rate; therefore, it was determined by extrapolation. The reactivity of halide ions dicreases in the series ($k_{ef} \times 10^4$, s^{-1}): F^- (251.42 ± 12.84) > NO_2^- (6.35 ± 0.34) > Cl^- (0.75 ± 0.03) > Br^- (0.33 ± 0.02) > I^- (0.25 ± 0.02).

The mechanism of dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes with halide ions was simulated by quantum chemical calculations of the structures of the initial reactants, prereaction complexes, transition states, and final products. The probability of E1cb and E2 mechanisms was estimated by preliminary DFT B3LYP/6-31G++(*d*,*p*) calculations in the ENERGY mode with inclusion of solvent effects (DMF) in terms of the polarizable continuum model (PCM). These mechanisms imply initial attack of the anionic reagent on the $Ar_2C\underline{H}$ hydrogen atom. The distance between the reagent and CH carbon atom was fixed at 3 Å. Successive extension of the C–H distance

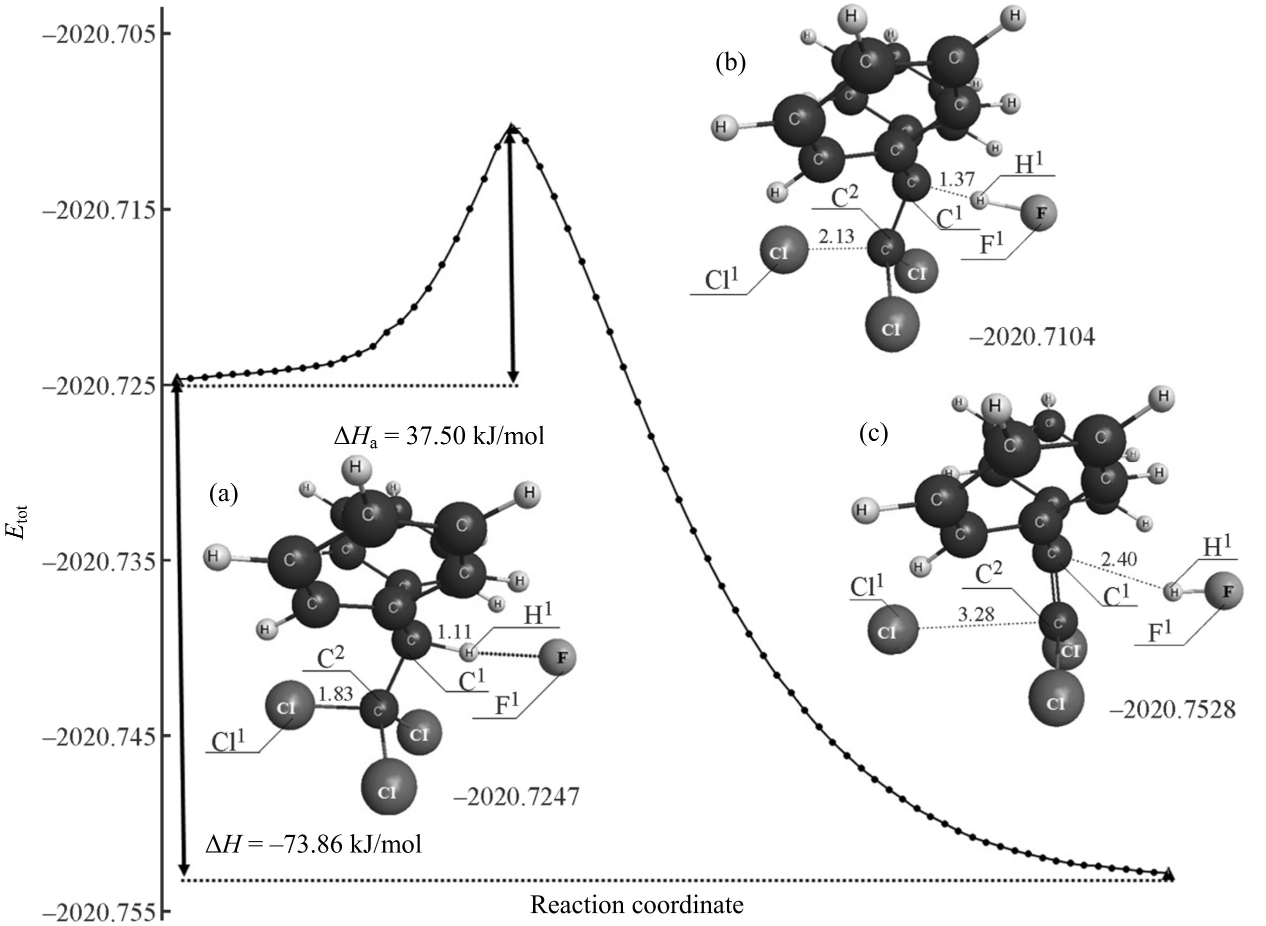


Fig. 1. Energy profile for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane with fluoride ion (interatomic distances are given in Å): (a) prereaction complex, (b) transition state, (c) products.

with a step of 0.05 Å (without subsequent optimization) was accompanied by increase of the total energy to a certain maximum value, and then the energy decreased. The structure corresponding to that maximum was taken as starting point in the search for transition states via gradient optimization. Taking into account the results obtained, in the further treatment we considered only attack of reagents on the $Ar_2C\underline{H}$ hydrogen atom of the substrate in keeping with the E2 or E1cb mechanism.

As follows from the kinetic data, fluoride ion is the most reactive among halide ions. As an example, Fig. 1 shows the energy profile of the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane with fluoride ion. Movement of H^1 toward the fluoride ion (Fig. 1a) leads to the transition state (Fig. 1b) whose Hessian matrix contains only one imaginary frequency corresponding to the linear oscillation of H^1 between C^1 and F^1. Descent along the intrinsic reaction coordinate (IRC) leads to prereaction complex or products (1,1-dichloro-2,2-diphenylethene, hydrogen fluoride, and chloride ion). The transition state is characterized by considerable elongation of the C^2–Cl^1 bond (to 2.13 Å against 1.83 Å for all three C^2–Cl bonds in the prereaction complex). As the H^1 moves apart, the C^2–Cl^1 distance synchronously increases to 3.28 Å due to sp^3–sp^2-rehybridization of the corresponding carbon atom with formation of 1,1-dichloro-2,2-diphenylethene (Fig. 1c).

We previously showed that 2,2-diaryl-1,1,1-trichloroethanes exist in antiperiplanar conformation; in the transition state formed by 2,2-diaryl-1,1,1-trichloroethanes with nitrite ion all five O···H···C–C–Cl atoms appear in one plane [3]. Analogous stereochemical structure was found for the transition states in the reactions of 1,1,1-trichloro-2,2-diphenylethane with halide ions. The torsion angle in the transition state for all structures and reagents varies within 3°.

Figure 2 shows the energy profile for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane with

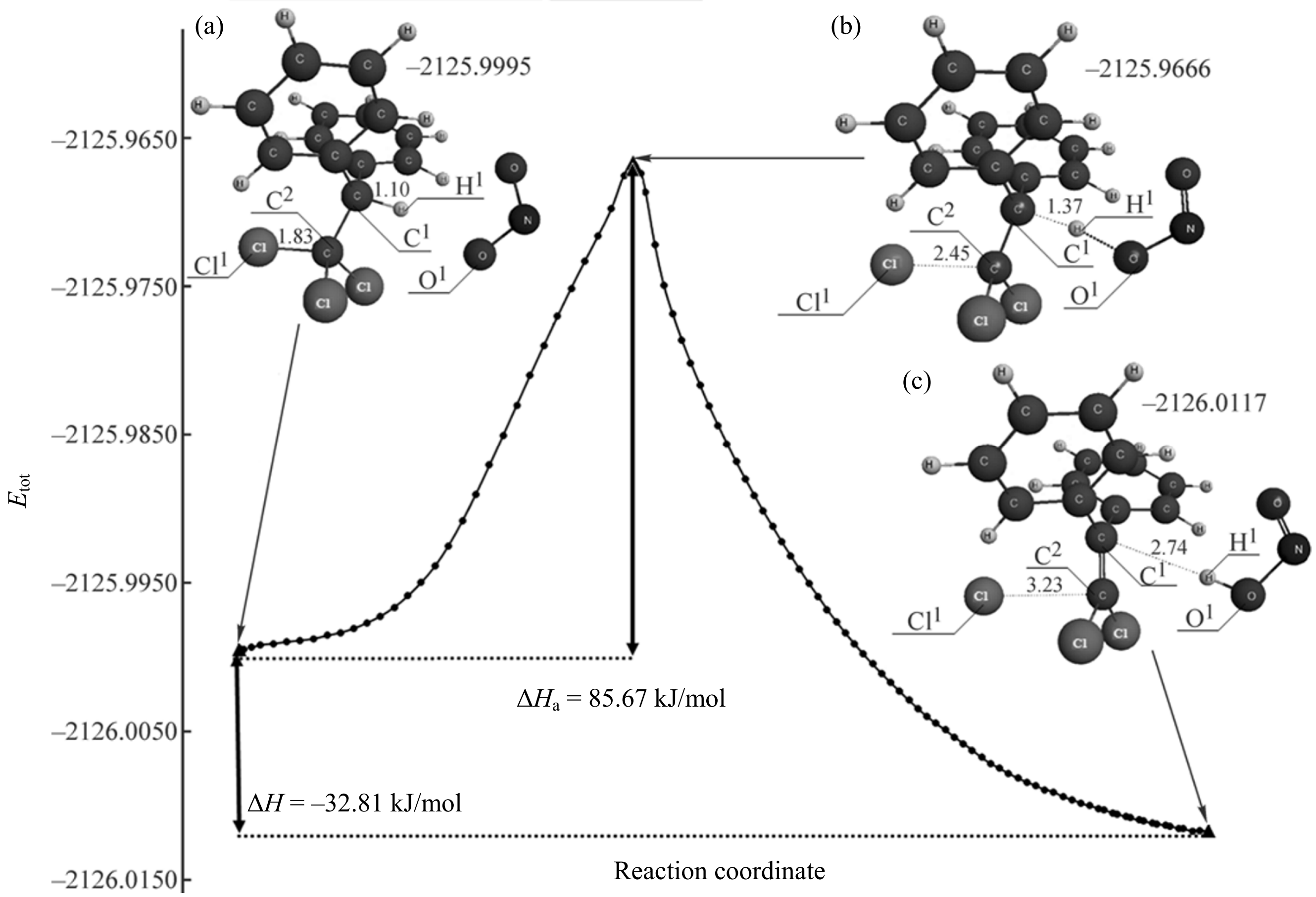


Fig. 2. Energy profile for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane with nitrite ion (interatomic distances are given in Å): (a) prereaction complex, (b) transition state, (c) products.

nitrite ion. Analysis of the transition states with fluoride and nitrite ions revealed changes of the distance between the departing Cl^1 atom and C^2 (2.13 and 2.45 Å), as well as of the H^1–C^1 distance (1.25 and 1.42 Å). The shorter distance between the reaction centers and more compact structure of the transition state with fluoride ion corresponds to the lower energy barrier in comparison to nitrite ion. The calculated enthalpy of activation (37.50 kJ/mol) confirms higher reactivity of fluoride ion relative to nitrite ion (85.67 kJ/mol). This may be rationalized by the reagent structure since fluoride ion is characterized by the smallest atomic radius among halide ions, so that it is capable of approaching the substrate most closely.

The results of quantum chemical simulation of the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane according to the E2 and E1cb mechanisms indicated bimolecular character of the process, specifically synchronous elimination of chlorine and hydrogen atoms from the α- and β-carbon atoms, almost planar arrangement of the Hlg···H···C–C–Cl pentad in the transition state (Fig. 1b) (this is a stereochemical condition for E2 mechanism), and single-step process typical of E2 mechanism (one maximum on the potential energy profile) (Scheme 1).

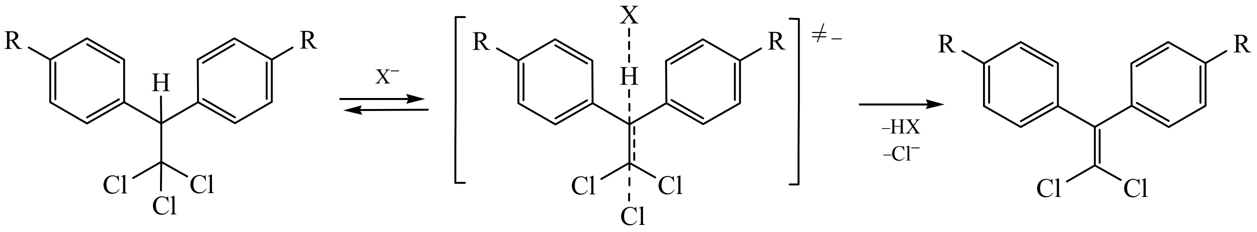
Thus, the results of our kinetic and theoretical studies in combination with our previous data [3] led us to conclude that the dehydrochlorination of 2,2-diaryl-1,1,1-trichloroethanes with alkali metal nitrites and halides in dipolar aprotic solvents follows E2 bimolecular elimination mechanism.

EXPERIMENTAL

2,2-Diaryl-1,1,1-trichloroethanes and 2,2-diaryl-1,1,1-trichloroethens were synthesized according to the procedures described in [5, 6].

The kinetic measurements were performed using a glass reactor equipped with a stirrer, reflux condenser, thermometer, and gas-inlet capillary for nitrogen. The reactor was charged with a solvent and substrate, the

Scheme 1.



R = H, Cl, NO_2, OEt, Me, OCMe; X = F, Cl, Br, I, NO_2.

mixture was adjusted to a required temperature with an accuracy of ± 0.5°C, and a required amount of the reagent was added with stirring. Samples of the reaction mixture were withdrawn during the reaction, cooled, and analyzed by GLC (Clarus 680 chromatograph equipped with a flame ionization detector; capillary column, 30 m × 0.32 mm; stationary phase 5% of diphenyl- and 95% of dimethylpolysiloxane; injector temperature 270°C, oven temperature 250°C, detector temperature 280°C; carrier gas nitrogen, flow rate 2.1 mL/min; hydrogen flow rate 45 mL/min, air flow rate 450 mL/min) and HPLC.

Quantum chemical calculations (geometry optimization and calculation of thermodynamic parameters) were performed at the DFT B3LYP/6-31G++(*d*,*p*) level of theory using Firefly program with account taken of solvent effects (DMF) in terms of the polarizable continuum model (PCM).

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