## Reactivity of Substituted Benzoic Acids and Their Complexes with 2,4,6-Trinitrotoluene toward Diphenyldiazomethane

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> > Received January 27, 2016

**Abstract**—The reactions of 2,4-dihydroxybenzoic and 4-aminobenzoic acids with diphenyldiazomethane are accelerated in the presence of 2,4,6-trinitrotoluene as  $\pi$ -acceptor. The catalytic effect of the latter is determined by the formation of charge-transfer complexes with the acids, which facilitates proton abstraction and stabilizes the corresponding anions.

DOI: 10.1134/S1070428016040059

It is known that formation of strong donor-acceptor complexes by organic and inorganic compounds dramatically changes chemical properties of the components due to redistribution of electron density in their molecules [1]. It is much more difficult to obtain experimental proofs for variation of the reactivity of compounds involved in weak  $\pi,\pi$ -complexes or charge-transfer complexes (CTC) as compared to the free species. Charge-transfer complexes are formed via electron transfer from the HOMO of the donor molecule to the LUMO of acceptor; however, insofar as the degree of charge transfer is usually not high, such adducts are considerably weaker than those formed via dative covalent bonding. Therefore, most  $\pi,\pi$ -complexes decompose partially or completely by the action of nucleophiles or electrophiles and even some solvents before chemical reaction. Penn and Lin [2] reported that the complexation of benzyl phenyl ethers with 2,3-dichloro-5,6-dicyanobenzoquinone facilitates cleavage of the C-O bond in the former. As noted in [3], acetolysis of 2,4,7-trinitrofluoren-9-yl p-toluenesulfonate and hydrolysis of 4-nitrobenzyl bromide are accelerated in the presence of various  $\pi$ -donors (such as phenanthrene) capable of forming CTC with the substrate. Another example is *cis*-*trans* isomerization of 4-nitrostilbene in the complex with *N*,*N*-dimethyl-aniline [4].

We previously showed that  $\pi$ - $\pi$  complexation of heteroaromatic *N*-oxides with such electron-deficient compounds as haloanils and tetracyanoethylene facilitates nucleophilic substitution in the aromatic ring and in some cases enables those reactions which are impossible with the free substrates [5, 6].

In this work we studied the reactions of substituted benzoic acids 1a-1c, as well as of their charge-transfer complexes with 2,4,6-trinitrotoluene (2), with diphenyldiazomethane (3) in toluene-dioxane (4:1), which afforded esters 4a-4c (Scheme 1).

2,4,6-Trinitrotoluene (2) is a fairly strong  $\pi$ -acceptor, whereas acids **1a** and **1b** exhibit electron-donating properties due to the presence of hydroxy or amino



groups in the aromatic ring. Acids 1a and 1b with 2 form  $\pi$ -complexes which exist in solution as equilibrium mixture with the free components. The complexes can be detected by spectrophotometry by the appearance of a charge transfer band at  $\lambda$  420–480 nm, which overlaps the absorption band of 2. The light vellow color of a solution of 2 strengthened on addition of acid 1a or changed to greenish yellow on addition of 1b. The absorbance of 2 at  $\lambda$  460 nm decreased to almost zero, so that it was possible to determine quantitative characteristics of the complexes by the Beneshi-Hildebrand method [7]. For this purpose, the dependence  $c_a L/D = f(l/c_d)$  was plotted, where  $c_{\rm a}$  and  $c_{\rm d}$  are the concentrations of the acceptor and donor, respectively, D is the optical density, and L is the cell path length (cm). The resulting plots were straight lines with a correlation coefficient of 0.99. The linear character of these plots indicated 1:1 stoichiometry of the CTCs, and their stability constants and molar absorption coefficients at the CTB maximum  $(\lambda 460 \text{ nm})$  were calculated from the coefficients of the linear equations:  $1a \cdot 2$ :  $K_{st} = 0.71$ ,  $\varepsilon_{460} = 24$ ;  $1b \cdot 2$ :  $K_{\rm st} = 4.50$ ,  $\varepsilon_{460} = 56$ . Thus, complex **1b** · **2** is much more stable than  $1a \cdot 2$  due to the presence of a very strong electron-donating substituent, amino group, in the *para* position of the benzene ring of **1b**. We failed to detect by spectrophotometry CTC of 2,4,6-trinitrotoluene with acid 1c containing an electron-withdrawing nitro group.

The formation of CTCs with  $\pi$ -acceptor 2 was expected to enhance proton-donating ability of acids 1a and 1b due to stabilization of negative charge in the respective anions. This assumption was verified by comparing the reactivities of 1a and 1b and their CTCs with 2 in the reaction with diphenyldiazomethane (3). It is known that aliphatic diazo compounds (alkyl- and aryldiazomethanes) are sensitive to acids, and they are sometimes used for quantitative assessment of proton-

Apparent rate constants for the reactions of acids 1a-1c with diphenyldiazomethane (3) in toluene–dioxane (4:1) at  $20^{\circ}C^{a}$ 

Acid	Concentration of 2, M	$k, \mathrm{s}^{-1}$
1a	0.000	$(1.74\pm0.04)\times10^{-3}$
<b>1</b> a	0.040	$(2.11\pm0.08)\times10^{-3}$
<b>1</b> a	0.060	$(3.05\pm0.07)\times10^{-3}$
1b	0.000	$(7.79\pm0.07)\times10^{-5}$
1b	0.040	$(9.96\pm0.11)\times10^{-5}$
1c	0.000	$(2.28\pm0.04) imes10^{-4}$
1c	0.040	$(2.47\pm0.05)\times10^{-4}$

<sup>a</sup> Concentration of **1a–1c** 0.045 M; concentration of **3** 0.0045 M.

donor properties of various compounds. Diazoalkanes react with acids to give the corresponding esters. The rate-determining step in this reaction is protonation of diazo compound with formation of unstable diazonium ion [8]. The use of diphenyldiazomethane is advantageous due to its intense color, so that the reaction rate can be monitored by spectrophotometry at  $\lambda$  525 nm. Trinitrotoluene 2 did not react with 3: the optical density of a solution containing compounds 2 and 3 did not change over several hours.

The reactions of acids 1a-1c with diphenyldiazomethane 3 in the absence of  $\pi$ -acceptor 2 were carried out at a 1-to-3 molar ratio of 10:1. In this case, the process may be considered to be pseudo-unimolecular, and it can be described by first-order kinetic equation. The apparent rate constants (see table) were calculated by Eq. (1):

$$k = 1/\tau \ln(D_0/D),$$
 (1)

where  $D_0$  and D are the optical densities at the initial moment and at a time  $\tau$ . The reaction with acid **1a** was characterized by the highest rate; obviously, intramolecular hydrogen bond involving the 2-hydroxy group increases the proton-donor power of **1a**. Acid **1c** reacted with **3** at a higher rate than **1b**, which is consistent with electron-withdrawing effect of the nitro group in the former.

The reactions of acids 1a-1c with diphenyldiazomethane (3) in the presence of  $\pi$ -acceptor 2 were studied under analogous conditions. The concentration of 2, as well as of acids 1a and 1b, considerably exceeded the concentration of 3. The apparent catalytic rate constants were also calculated by Eq. (1). As follows from the data in table, addition of  $\pi$ -acceptor 2 accelerated the reaction, especially with acids 1a and 1b. The reaction rate also significantly increased as the concentration of 2,4,6-trinitrotoluene changed from 0.04 to 0.06 M, as shown with acid 1a as an example. The catalytic effect of 2 in the reaction with acid 1cwas weaker than in the case of 1a or 1b since the CTC of 1c with 2 is very unstable (if formed).

Obviously, two concurrent processes are possible in the system benzoic acid– $\pi$ -acceptor–diazo compound: catalytic and noncatalytic. However, it is difficult to rigorously determine the kinetics of the catalytic reaction without elucidating its mechanism. Most probably,  $\pi$ -acceptor forms a complex with acid **1**, which facilitates deprotonation of the latter, i.e., it acts as an electron-withdrawing substituent but is not covalently bound to the aromatic ring. Such  $\pi$ -acceptors as chloranil or tetracyanoethylene cannot be used in the examined reactions, since they react themselves with diazo compound **3**.

## EXPERIMENTAL

The electronic absorption spectra of pure compounds were recorded on an SF-56 spectrophotometer in the range  $\lambda$  400–600 nm, and the optical densities of reaction mixtures were measured on a Portlab 501 spectrophotometer (cell path length 1 cm). The charge transfer complexes of 2,4,6-dinitrotoluene (2) with acids 1a and 1b were studied by the Benesi-Hildebrand method at 20°C in toluene-dioxane (4:1) at the following concentrations of the components, M: 1a · 2:  $c_2 = 0.05, c_{1a} = 0.075, 0.100, 0.125, 0.150, 0.175;$ **1b**  $\cdot$  **2**:  $c_2 = 0.02$ ,  $c_{1b} = 0.02$ , 0.03, 0.04, 0.05, 0.06. A solution of diphenyldiazomethane was prepared by oxidation of benzophenone hydrazone with lead(IV) oxide in toluene; its concentration was determined by spectrophotometry at  $\lambda$  525 nm ( $\varepsilon_{525} = 100$ ). The kinetic studies of the reactions of acids 1a and 1b with diazo compound 3 were carried out at 20°C. In all cases, the concentration of 3 was 0.0045 M, and of acids 1a-1c, 0.045 M; the concentration of 2 was 0.04 or 0.06 M (see table).

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REACTIVITY OF SUBSTITUTED BENZOIC ACIDS AND THEIR COMPLEXES

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