

THERMAL HYDROGEN TRANSFER FROM ALCOHOLS TO TETRACYANOETHYLENE

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Hydrogen transferred thermally from several organic compounds such as alkylarylcarbinols, tetrahydroquinoline, and 2,5-dihydrofuran to tetracyanoethylene. The mechanism of the hydrogen transfer from the alcohols was investigated.

The thermal hydrogen transfer from some kind of organic compounds to high-potential quinones is well known.<sup>1)</sup> However, the reports of the hydrogen transfer to olefins are scarce.<sup>2-4)</sup> As the reaction of tetracyanoethylene (TCNE), the dehydrogenation of 1,4-dihydrobenzenes<sup>3)</sup> and 9(11)-dehydroergosteryl acetate<sup>4)</sup> has been reported.

During the course of the investigation of the catalytic hydrogen transfer from organic compounds to olefins,<sup>5)</sup> we found that TCNE dehydrogenated several organic compounds without catalysts. For examples, when 2,5-dihydrofuran, 1,2-dihydronaphthalene, tetrahydroquinoline, or 1-phenylethanol (0.4 M) was heated along with TCNE (0.4 M) in dichloromethane at 140°C for 3 hr, furan, naphthalene, quinoline, or acetophenone was detected in 95, 47, 43, or 35% yield, respectively, by glc analyses. From the reaction mixtures, a white crystalline product was isolated and identified as 1,1,2,2-tetracyanoethane by the comparison with an authentic sample.<sup>6)</sup> In the reaction of the alcohol or the amine, side reactions are inferred to occur, because the total amount of the remaining hydrogen donor and the dehydrogenated material was smaller than the initial amount of the donor. It has been reported that TCNE undergoes substitution reactions with alcohols<sup>7)</sup> and amines.<sup>7,8)</sup> The side reactions described above are considered to be such substitution reactions.

The dehydrogenation of alcohols was studied in details. When 0.4 M phenylcarbinols, PhCH(OH)R, and 0.4 M TCNE were heated for 3 hr in dioxane, the corresponding carbonyl compounds were obtained (Table). The yield of the products was highest when R was Me, and side reactions were intensive when R was H or Ph. All the experiments described hereafter were carried out under the condition that phenylethylcarbinol and TCNE were heated at 100°C in dioxane, because no side reaction was observed under this condition.

The initial rate of the reaction increased considerably by the addition of polar compounds such as acetonitrile, nitrobenzene, acetophenone, and hydroquinone. The addition of benzoyl peroxide did not promote the reaction. These observations suggest that the hydrogen transfer does not proceed via a radical process but via an ionic one. The rate showed the first-order dependence on the concentration of the donor and the acceptor, respectively. The values of the observed rate constant,  $k_{\text{obs}}$ , of the deuterated donor, PhCD(OD)Et and PhCH(OD)Et, were  $1.5 \times 10^{-3}$  and  $5.7 \times 10^{-3} \text{ mol}^{-1} \text{ l min}^{-1}$ , respectively, while that of PhCH(OH)Et was  $5.6 \times 10^{-3} \text{ mol}^{-1} \text{ l min}^{-1}$ . This fact indicates

Table. Hydrogen Transfer from  
PhCH(OH)R to TCNE.

R	Temp., °C	Yield of PhCOR, %	Recovered alcohol, %
H	100	10	57
	120	22	57
Me	100	35	47
	120	57	16
Et	60	6	84
	100	25	77
	120	54	38
Pr <sup>i</sup>	100	9	83
	120	26	57
Ph	100	30	22
	120	37	17

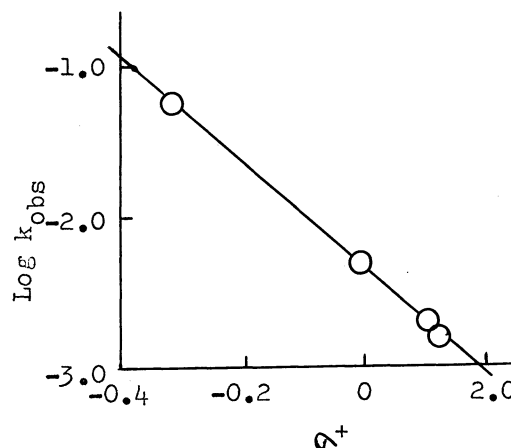
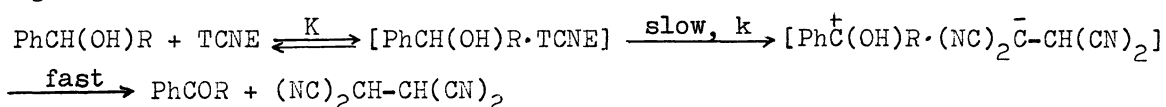


Fig. Log  $k_{\text{obs}}$  vs  $\sigma^+$

that the transfer of the hydrogen atom attached on  $\alpha$ -carbon atom of the alcohol is rate-determining and the hydrogen atom of the hydroxyl group transfers fast. In the reaction of  $p$ -substituted donor,  $p\text{-X-C}_6\text{H}_4\text{CH(OH)C}_2\text{H}_5$ , logarithm of  $k_{\text{obs}}$  was linearly correlated with  $\sigma^+$  rather than  $\sigma$  and  $\rho$  was  $-0.32$  (Fig.). As  $k_{\text{obs}}$  may be the product of the equilibrium constants of the charge transfer complex formation<sup>9)</sup> and the rate constants of the rate-limiting step, the  $\rho$  constant, which is negative and has relatively small value, suggests that the hydrogen donors are positively charged and the charge separation is not so strong in the charge transfer complexes and/or the transition state of the rate-limiting step.

Based on these facts we propose the following two step ionic process for this hydrogen transfer reaction.



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