[CONTRIBUTION FROM THE WASHINGTON UNIVERSITY, SAINT LOUIS, MISSOURI]

Effects of Ion Association on Rates of Oxidation–Reduction Transfer Reactions in the Naphthalene–Naphthalenide Systems[1]

BY P. J. ZANDSTRA AND S. I. WEISSMAN

RECEIVED JUNE 8, 1962

The rates of the rapid reactions

$$C_{10}H_8^- + C_{10}H_8 = C_{10}H_8 + C_{10}H_8^- \qquad (1)$$

$$C_{10}H_8^-Na^+ + C_{10}H_8 = C_{10}H_8 + Na^+C_{10}H_8^- \qquad (2)$$

have been measured in tetrahydrofuran, tetrahydropyran and 2-methyltetrahydrofuran. The processes follow a second order kinetic law. The rates and their variation with temperature depend on solvent: (1) is generally more rapid than (2), but in tetrahydrofuran the rate of (2) increases with decreasing temperature below 300°K. and is greater than the rate of (1) below 280°K.

Introduction

An earlier kinetic study[2] of the reaction between naphthalenide ion and naphthalene was unable to make a direct distinction between the reactions

$$C_{10}H_8^- + C_{10}H_8 = C_{10}H_8 + C_{10}H_8^- \qquad (1)$$

$$C_{10}H_8^-Na^+ + C_{10}H_8 = C_{10}H_8 + Na^+C_{10}H_8^- \qquad (2)$$

Refinements of the experimental methods now permit studies of the individual processes 1 and 2 in several solvents. The spectrum of the naphthalenide ion $C_{10}H_8^-$ displays 25 well resolved lines. In the ion pair $Na^+C_{10}H_8^-$ each line is split into 4 components of equal intensities with a splitting which increases with temperature. The spectrum of a mixture corresponding to the equilibrium

$$C_{10}H_8^- + Na^+ = C_{10}H_8^-Na^+ \qquad (3)$$

is a superposition of the two spectra with the intensity ratio determined by the relative concentrations of the two paramagnetic species.[3] In these solvents the rates of (3) are so slow that no perturbations of the spectra by the interconversion occur. The temperature ranges and the concentrations used in determining the exchange rates for reactions 1 and 2 were chosen in such a way that a few well resolved lines corresponding to each of the paramagnetic species were present with sufficient intensities at the center of the spectrum.

We have found that the rate constants, dissociation constants, and sodium coupling constants in the solvents tetrahydrofuran, 2-methyltetrahydrofuran, and tetrahydropyran lie in ranges which permit measurements of the reactions 1 and 2.

Experimental

Reduction of naphthalene to naphthalenide was carried out by procedures already described.

Each set of measurements was made in a sealed-off apparatus which included a cell for optical absorption measurements and one for e.s.r. measurements. Known amounts of naphthalene contained behind break seals were added to the solution. Before addition of naphthalene the line breadths of the radical solution were determined over the temperature ranges to be covered. The concentration of radical was monitored by the optical absorption. Each line broadening used for determination of rates is a difference between a breadth in the presence of added naphthalene and the breadth in the absence of naphthalene at the temperature in question.

Results and Discussion

In each of the systems which we have measured the line broadening at constant temperature is proportional to concentration of naphthalene and independent of concentration of naphthalenide. The process is, therefore, first order with respect to each of the reactants and is appropriately described by a second order rate constant.

Table I contains a summary of the results. Arrhenius plots for tetrahydropyran and 2-methyltetrahydrofuran are normal with slopes corresponding to the activation energies in Table I. Plots of log k *vs.* $1/T$ for reactions 1 and 2 in the tetrahydrofuran are given in Fig. 1.

TABLE I

Solvent	Species	"Activation energy," kcal./mole	Temp., °C.	$k \times 10^{-6}$ M^{-1} sec.$^{-1}$
Tetrahydropyran	Ion pair	17.6 ± 0.9	21	4.4 ± 0.1
	Ion	18.5 ± 2.2	−23	9.7 ± 4.5
2-Methyltetrahydrofuran	Ion pair	12.4 ± 3.6	21	4.5 ± 0.1
	Ion	12.8 ± 3.2	−23	2.8 ± 0.7
Tetrahydrofuran	Ion pair	4.6 ± 0.5	50	34.0 ± 8
		−6.8 ± 0.5	−16	71.0 ± 15
	Ion	13.2 ± 1.5	13	38.0 ± 14

In all the solvents except tetrahydrofuran at low temperature the rate constant of the transfer process involving the ion pair is lower than the one involving the dissociated ion. The temperature coefficients of the two rates in a particular solvent are not greatly different but they vary markedly from solvent to solvent. In tetrahydrofuran the rate constant of the process involving the ion pair increases with decreasing temperature below 300°K. and ultimately becomes greater than the rate constant for the reaction with the dissociated naphthalenide ion.

The spectra of Fig. 2 display the difference in rates in tetrahydrofuran at −20°. The central peak arises from dissociated ions, the two flanking peaks from ion pairs. In the upper spectrum, obtained from a solution containing naphthalene at $0.6 \times 10^{-2}M$, the interval between points of extreme slope for the lines of the ion pair is slightly greater than for the line of the dissociated ion. Increase of naphthalene concentration to 2.8×10^{-2} M produces no observable increase in the breadth of the line of the dissociated ion and an increase of about fifty per cent. in the breadth of the lines of the ion pair. The latter increase is seen both in the increased interval between points

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(1) This work has been supported by the United States Air Force under contract, the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and an equipment loan contract with O.N.R.

(2) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957).

(3) N. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961).

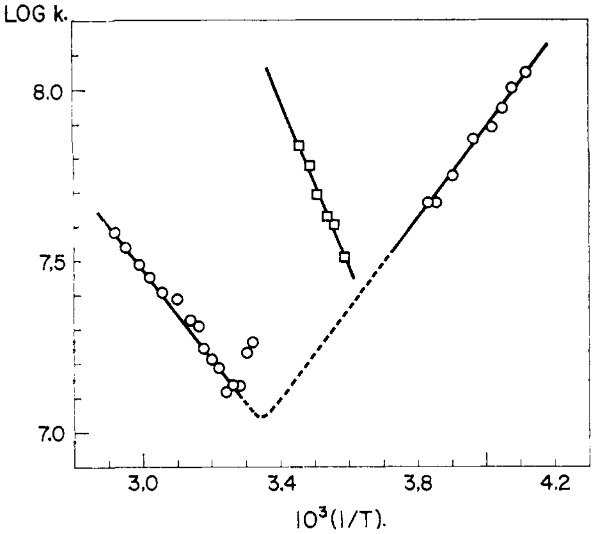

Fig. 1.—Log k *vs.* $1/T$ in tetrahydrofuran, k in M^{-1} sec.$^{-1}$. The circles are measured points for the ion pair, the squares for the free ion.

of extreme slope and decreased amplitude of the lines.

We note first that the process involving the ion pair must involve transfer of the sodium ion as well as electron spin from one naphthalene to another. Consider two possible processes

$$C_{10}H_8^-Na^+ + C_{10}H_8 = C_{10}H_8 + Na^+ + C_{10}H_8^- \quad (2')$$

$$C_{10}H_8^-Na^+ + C_{10}H_8 = C_{10}H_8 + Na^+C_{10}H_8^- \quad (2)$$

The first process provides a path for dissociation of the ion pair. Detailed balancing requires that the ratio of rate constants of forward and backward processes described in (2′) be equal to the dissociation constant. The dissociation constants are in the range 10^{-6}–10^{-5} M and the rate constants in the range 10^6–10^8 M^{-1} sec.$^{-1}$. Hence termolecular rate constant for the reaction from right to left of the order 10^{11}–10^{14} M^{-2} sec.$^{-1}$ would be required. Reaction 2′ is thus excluded.

It is clear from the data that the solvent plays an important role both for the transfer processes involving dissociated ions and for those involving ion pairs.

The bizarre behavior of the ion pair in tetrahydrofuran has led us into a fruitless quest for processes other than the chemical exchange to which the line broadening might be attributed. Consider, for instance, the possibility that the anomaly is associated with a rapid increase in viscosity with decreasing temperature and consequent increase in contribution of the anisotropic components of the g tensor and hyperfine tensor to the broadening. In the absence of naphthalene neither the dissociated ion nor ion pair exhibits anomalies in the dependence of line breadth on temperature. In the presence of naphthalene only the ion pair exhibits the anomaly. Hence, increasing local viscosity about ion pairs with addition of naphthalene would be required. Only some sort of selective clustering of naphthalene molecules about ion pairs would seem to be capable of producing such an effect. Consider first the requirements if the clusters were long lived. Monodisperse clusters at all concentrations of added naphthalene would be required since the lines of the ion pair are simple Lorentzian in shape with a single breadth in each solution. Further, the monodisperse clusters would be required to change in properties with concentration of naphthalene so as to produce the observed linear dependence of line breadth with concentration. While we cannot exclude this possibility completely, we can find no reasonable set of equilibria which can produce it.

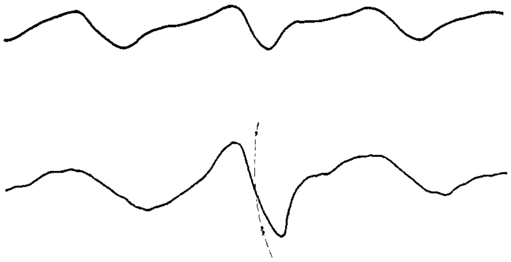

Fig. 2.—Central portion of dX''/dH *vs.* H for a mixture of $C_{10}H_8^-$ and $Na^+C_{10}H_8^-$ in tetrahydrofuran at −20°: upper spectrum with $C_{10}H_8$ at 0.6 × 10^{-2} M; lower spectrum with $C_{10}H_8$ at 2.8 × 10^{-2} M.

Another possibility in which the ion pairs are found in clustered environments with lines too broad for observation and in normal environments with occasional exchange between the two retains the difficulty we are trying to avoid. The breadth in this case is determined by the rate and we again have a process whose rate increases with decreasing temperature.

A final possibility in which the environments are polydisperse with such rapid averaging among them that the observed line breadths are averages over the various environments require impossibly high rate constants for interconversion among the environments.

A pre-equilibrium could yield an anomalous sign of temperature coefficient but it cannot easily account for the change in sign.

A clue may be provided by the large variation in sodium coupling constant of the ion pair with temperature in THF. The variation has been ascribed to the temperature dependence of occupation probabilities of vibrational state associated with motion of sodium ions relative to the rings in the ion pairs.[3] Assignment of different rate constants for the transfer reactions to the vibrational states of the ion pair with the greater rate constants belonging to the lower states can lead to the anomalous temperature dependence.

The situation is illustrated by the behavior of a model in which the process may occur *via* two vibrational states. Let k_1 and k_2 be the rate constants for the lower and upper states, respectively, g_1 and g_2 their statistical weights and ΔE the energy interval between them. If the rate of equilibration between the vibrational states is rapid compared with the rate of the transfer process, the over-all rate constant k is given by $k = (k_1 + k_2K)(1 + K)^{-1}$ where $K = (g_2/g_1)e^{-\Delta E/kt}$. If $g_2 >> g_1$, at high temperature $k = k_2$ and at low temperature $k = k_1$. If the rate constant k_1

is large compared with k_2 the rate at low temperature may be higher than the rate at high temperature.

We note that the preceding suggestion bears some relation to another process in which rates increase with decreasing temperature, the electrical conductivity of metals. Here the transmission of electrons increases with decreasing temperature because of decreased scattering by the vibrations of the environment.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MD.]

Tracer Studies with Carbon-14. I. Some of the Secondary Reactions Occurring during the Catalytic Cracking of *n*-Hexadecane over a Silica–Alumina Catalyst

BY W. ALEXANDER VAN HOOK[1] AND PAUL H. EMMETT

RECEIVED MAY 31, 1962

Some secondary reactions in the *n*-hexadecane–aluminosilicate system at 372° have been examined in an integral reactor with carbon-14 tracers in the presence of an inert helium diluent. The reactions of the primary products propylene, propane, *n*-butane, 1-heptene and *n*-heptane were traced and their importance in determining the final product distribution assessed. Product and radioactivity analyses were made through carbon number twelve with the use of gas chromatography and static (carbon dioxide) counting, respectively. The results may be briefly summarized by pointing out that the tracer olefins, propylene and heptene, undergo as secondary reactions very extensive alkylation, isomerization, polymerization and cracking during the cracking of the hexadecane. Propylene seems to play an important part in the formation of aromatics and also in the formation of the higher saturated C_8- to C_{12}-hydrocarbons. On the other hand, the saturated tracer hydrocarbons propane, *n*-butane and *n*-heptane are relatively inactive during the hexadecane cracking runs and come through the reactor almost unchanged.

Introduction

The carbonium ion theory of catalytic cracking independently proposed by Greensfelder, Voge and Good[2] and by Thomas[3] in 1949 is now generally accepted by most workers in the field. The primary cracking products of any pure hydrocarbon feed predicted by the theory are, however, to some extent obscured by the products of the secondary reactions of the olefins and paraffins formed in the reaction. These secondary reactions include isomerization, hydrogenation, alkylation, polymerization and aromatization. The last of these reactions (aromatization) is not clearly understandable in the light of the present carbonium ion theory,[4] although the others follow as a direct consequence of the reactions of carbonium ions. In this paper are presented and discussed the results of some tracer experiments in which the quantitative importance of the secondary reactions, polymerization, isomerization, alkylation and cracking of some of the primary products have been assessed, and in which evidence is obtained relative to the plausible routes of aromatic formation.

In these experiments small amounts (0.06 mole % of gases, 0.9–1.5 mole % of liquids) of tagged primary products including propylene, propane, heptene-1, *n*-heptane and *n*-butane were mixed with a stream of *n*-hexadecane and helium and passed at 372° through an integral reactor filled with cracking catalyst. The products were analyzed gas chromatographically and counted.

Such a technique has been previously utilized by Andrianova and co-workers[5–8] in studies of isooctane cracking. However, their results are not amenable to precise interpretation because the inordinately high tracer to reactant ratios used by them lead to the suspicion that the steady state conditions on the catalyst surface were seriously affected by the added tracer compounds. Furthermore, analysis of their products was complete only through carbon number five; radioactive analysis of the higher cuts, including aromatics, were then grouped and averaged.

Experimental

Reactor System.—The apparatus consisted of helium carrier gas supplies, a hexadecane bubble saturator, trace injector systems for gases and liquids, the reactor itself and finally the product traps. Catalyst regeneration and coke analysis trains were also provided. The system was made of Pyrex.

Helium (stream I) was bubbled through the hexadecane saturator at about 215° after which it was joined in a heated transfer line by a second helium carrier flow (stream II) which had already passed through the tracer injector system. This last, for gaseous tracers, consisted of a motor-driven mercury leveling device made from 2-mm. capillary tubing fitted at the top with a 0.1-mm. restriction 2 cm long. It metered 0.01 cc./min. S.T.P. of the gaseous tracer into helium stream II. For liquid tracers, a long narrow bubbler, thermostated at an appropriate temperature, was used for adding the tracer to stream II.

The helium–hexadecane–tracer mixture entered the reaction chamber in which 23.2 g. (37-cc. bulk volume) of Davison pelleted commercial cracking catalyst[9] was supported with a plug of glass wool. The 25-mm. (o.d.) Pyrex reactor tube was supported in a vertically mounted steel block furnace 6″ in diameter and 16″ long. A glass thermocouple well ran through the center of the catalyst

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[1] Abstracted from part of the Doctoral thesis of W. A. Van Hook.

[2] B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.* **41**, 2573 (1949).

[3] C. L. Thomas, *ibid.*, **41**, 2564 (1949).

[4] H. H. Voge, Chapter 5 of "Catalysis," Vol. 6, "Hydrocarbon Catalysis," edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1958.

[5] E. A. Andreev, T. I. Andrianova, B. V. Klimenok, O. V. Krylova, S. Z. Roginskii and M. M. Sakharov, *Doklady Akad. Nauk SSSR*. **96**, 781 (1954), cited from *C. A.*, **49**, 7230c (1955).

[6] E. A. Andreev, T. I. Andrianova, O. V. Krylova and M. M. Sakharov, *Doklady Akad. Nauk SSSR*, **102**, 1119 (1955).

[7] S. Z. Roginskii and T. I. Andrianova, *Zhur. Obshchei Khim.*, **26**, 2151 (1956), cited from *C. A.*, **51**, 3973i (1957).

[8] T. I. Andrianova and S. Z. Roginskii, "Problemy Kinetiki i Kataliza, Akad. Nauk SSSR, Inst. Fiz Khim.," Soveshchanie, Moscov, 1956, Vol. 9, pp. 152–161; *C. A.* **53**, 7743c (1958).

[9] The catalyst analysis, as given through the courtesy of W. R. Briggs, W. R. Grace Research Center, Clarkville, Md., was 13.21% Al_2O_3, 0.03% Fe, 0.30% SO_4, 0.02% Na_2O and 86.44% silica (by difference). The surface area was 540 m.²/g. and the pore volume 0.74 cc./g.