The authors wish to thank the Spanish Comisión Asesora de Investigación Científica y Técnica for subsidising the research reported in this article as part of an investigation into the mechanism of formation of carcinogenic N-nitroso compounds.

References

- [1] J. A. McCleverty, Chem. Rev. 79, 53 (1979).
- [2] R. Eisenberg and C. D. Meyer, Acc. Chem. Res. 8, 26 (1975).
- [3] F. Bottomley, Acc. Chem. Res. 11, 158 (1978).
- [4] N. G. Connelly, Inorg. Chim. Acta Rev. 6, 47 (1972).
- [5] F. Bottomley and M. J. Mukaida, J. Chem. Soc., Dalton Trans. 1982, 1933.
- [6] W. L. Bowden, W. F. Little, and T. J. Meyer, J. Am. Chem. Soc. 98, 444 (1976); ibid 99, 4340 (1977).
- [7] P. G. Douglas, R. D. Feltham, and H. G. Metzger, J. Am. Chem. Soc. 93, 84 (1971); P. G. Douglas and R. D. Feltham, ibid 94, 5254 (1972).
- [8] L. Dózsa, V. Kormos, and M. T. Beck, Inorg. Chim. Acta 82, 69 (1984).
- [9] A. R. Butler, C. Glidewell, J. Reglinski, and A. Waddon, J. Chem. Res. (S) 1984, 279.
- [10] J. Casado, M. A. López Quintela, M. Mosquera, M. F. Rodríguez Prieto, and J. Vázquez Tato, Ber. Bunsenges. Phys. Chem. 87, 1208 (1983).
- [11] N. T. Crosby and R. Sawyer, Adv. Food Res. 22, 1 (1976).
- [12] R. Bonnett, A. A. Charalambides, R. A. Martin, K. D. Sales, and B. W. Fitzsimmons, J. Chem. Soc., Chem. Commun. 1975, 884; R. Bonnett, S. Chandra, A. A. Charalambides, K. D. Sales, and P. A. Scourides, J. Chem. Soc., Perkin Trans. 1, 1980, 1706.
- [13] G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 2, p. 1511, 2nd ed., Academic Press, New York 1965.
- [14] J. H. Swinehart and P. A. Rock, Inorg. Chem. 5, 573 (1966).
- [15] N. E. Katz, M. A. Blesa, J. A. Olabe, and P. J. Aymonino, J. Inorg. Nucl. Chem. 42, 581 (1980).
- [16] H. Maltz, M. A. Grant, and M. C. Navaroli, J. Org. Chem. 36, 363 (1971).

- [17] D. J. Kenney, T. P. Flynn, and J. B. Gallini, J. Inorg. Nucl. Chem. 20, 75 (1961).
- [18] E. J. Baran, A. Müller, and N. Weinstock, An. Asoc. Quim. Argentina 59, 377 (1971).
- [19] H. E. Toma, A. A. Batista, and H. B. Gray, J. Am. Chem. Soc. 104, 7509 (1982).
- [20] B. C. Challis and A. J. Lawson, J. Chem. Soc. (B) 1971, 770.
- [21] J. Masek and H. Wendt, Inorg. Chim. Acta 3, 455 (1969).
- [22] J. H. Swinehart, Coord. Chem. Rev. 2, 385 (1967).
- [23] I. Murati, D. Pavlovic, A. Sustra, and S. Asperger, J. Chem. Soc., Dalton Trans. 1978, 500.
- [24] D. B. Soria, M. V. Hidalgo, and N. E. Katz, J. Chem. Soc., Dalton Trans. 1982, 1555.
- [25] Z. Bradic, M. Pribanic, and S. Asperger, J. Chem. Soc., Dalton Trans. 1975, 353.
- [26] A. N. Garg and P. N. Shukla, Z. Naturforsch. 36b, 59 (1981).
- [27] J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, J. Chem. Soc. (A) 1969, 1212.
- [28] S. S. Mirvish, J. Sams, T. Y. Fan, and S. R. Tannenbaum, J. Natl. Cancer Inst. 51, 1833 (1973).
- [29] P. R. Adby and M. A. H. Dempster, "Introduction to Optimization methods", Chapman and Hall, London 1974; S. D. Christian and E. E. Tucker, Int. Lab. 13, 106 (1983).
- [30] J. M. Antelo, F. Arce, J. Casado, M. Sastre, and A. Varela, J. Chem. Eng. Data 29, 10 (1984).
- [31] R. P. Bell, "The Proton in Chemistry", Chapman and Hall, London 1973.
- [32] W. S. Layne, H. H. Jaffe, and H. Zimmer, J. Am. Chem. Soc. 85, 435 (1963); ibid 85, 1816 (1963).
- [33] J. Masek, Inorg. Chim. Acta Rev. 3, 99 (1969).
- [34] M. Eigen, Angew. Chem., Int. Ed. Engl. 3, 1 (1964).
- [35] W. P. Jencks, Chem. Rev. 72, 705 (1972); J. M. Sayer and W. P. Jencks, J. Am. Chem. Soc. 95, 5637 (1973); W. P. Jencks and J. M. Sayer, Faraday Symp. 10, 41 (1975); W. P. Jencks, Acc. Chem. Res. 9, 425 (1976); W. P. Jencks, Acc. Chem. Res. 13, 161 (1980).

(Eingegangen am 13. Dezember 1984, endgültige Fassung am 18. März 1985) E 5918

Catalytic Dehydrochlorination of t-Butyl Chloride on Alkali Halides

N. Yoshida, O. Akebe, and S. Kishimoto

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan

Alkali Halide | Catalysis | Chemical Kinetics | Color Center | Elimination Reaction

Potassium bromide treated with bromine and chlorine vapor respectively, was used as catalyst for the dehydrochlorination of t-butyl chloride. The results indicated a clear correlation between the presence of color centers (V-centers) in the halides and their catalytic activity. The activation energies of the catalytic dehydrochlorination were measured.

Introduction

Since the work of Schwab and Noller, elimination reactions on metal halide catalysts have extensively been studied [1]. These reaction systems have also been used by many investigators in order to obtain the correlations between the defect structure of solids and the catalytic activity. Simkovich and Wagner [2] studied the dehydrochlorination of t-butyl chloride on AgCl doped with CdCl₂, and suggested that both ad-anion and cation vacancies facilitate the reaction. Hauffe and Sitabkhan [3] found for the same reaction when the surface of AgCl was treated with Cl₂ vapor, that the surface becomes catalytically active. Wiesendanger [4], Wise and Wood [5] found that changes in the defect structure (hole density) of CuI give rise to a measurable change in the catalytic activity for the decomposition of isopropyl iodide. Hall and Rase [6] reported that the increase in dislocation density in LiF with various treatments resulted in increased catalytic activity in the decomposition of ethanol. Recent detailed studies relating to the catalytic activity of non-stoichiometric copper chlorides have been published by Harrison and Ng [7]. Realizing these noteworthy results, we commenced a study of dehydrochlori-

nation of t-butyl chloride on NaCl treated with Na vapor [8]. The results indicated that the presence of F-centers in the crystal plays an important role in the catalytic reaction. On the other hand, V-centers have also been observed in several alkali halides treated under a variety of conditions [9, 10]. This paper deals, in detail, with the correlation between the presence of the V-centers in KBr and the catalytic activity for the same reaction. The reason for selecting this halide as a catalyst was that the V-centers can be readily formed by heating it in Br_2 vapor and that some centers are stable up to temperatures at which the catalytic measurements are made.

Experimental

t-Butyl chloride (Wako Pure Chem., Ltd.) was distilled at ordinary pressure. Gas chromatographic analysis showed less than 0.6% impurities and the purification was further carried out by distillation under reduced pressure. KBr was optical grade crystals obtained from the Horiba Ltd. The crystals were pulverized in an agate mortar. The powder was then placed in the reactor made of pyrex glass and prior to use, it was heated at 390° C for 1 hr under a vacuum of 10^{-6} Torr in order to remove adsorbed water and any influence of mechanical damage. It was observed by gravimetric measurement that above this temperature the sublimation of the specimen occurred rapidly. Br2 (Nakarai Chem., Ltd.) and Cl2 (Takachiho Chem., Co.) were respectively dried in P2O5 and CaCl2 traps and further purified by low temperature distillation. The surface area of the catalyst was determined from the adsorption of Kr at -196°C using a relation, $V_{\rm m} = V_{\rm mid}/0.58$, where $V_{\rm m}$ and $V_{\rm mid}$ respectively denote the monolayer capacity of the surface and the adsorbed amount of Kr at the midpoint of the step corresponding to two-dimensional condensation [11]. The rates of catalytic reactions were obtained by measuring the pressure increase in a closed reactor at reaction temperatures between 100 and 150 $^{\circ}\mathrm{C}$ and with initial pressures of 25 to 100 Torr. Greaseless stopcocks were used to connect the reactor with the other systems of apparatus. Poisoning of the catalyst by Hg vapor was avoided by using a Au foil trap between the reactor and a Hg manometer. At first, blank reactions with no catalyst were carried out and it was confirmed that no reactions occurred under the present experimental conditions.

V-center injection into the catalyst was done by exposure to Br_2 vapor of 100 Torr at temperatures of 135 to 380°C for 1 hr and then by quenching to room temperature. Previous studies have proposed, as models for these centers, the combination of cation vacancies and molecular halogen species [9,10]. The presence of the centers was confirmed qualitatively by the method presented by Hersh [12]. This method is a sensitive calorimetric test based on the conversion of excess of free halogen in the crystal into intensely absorbing complexes according to the reaction, $X_2 + X^-$ (aqueous) X_3^- (X is a halogen atom). The complex, Br_3^- has an absorption maximum at 270 nm. Therefore, after the Br-treatment, the sample was dissolved in water and the analysis of the complex was made in a usual manner using a spectrophotometer.

Results

The reproducibility of the catalytic reactions is shown in Fig. 1 for duplicated runs with the same catalyst at three temperatures. It is clear that the catalyst was not poisoned by the reaction products in the course of time under the present conditions.

It is well known that catalytic activities of solids, when subjected to mechanical treatments such as crushing or grinding, become different from the one intrinsic to the original crystal. For example, Schrader and Balarew [13] demonstrated the creation of the catalytic activity due to lattice defects generated in NaCl by grinding for the dehydrochlorination of i-propyl chloride. The grinding effect on the activity in the present experiments is shown in Table 1. The results indicate that no change in the specific activity occurred although the surface area was increased with the grinding time. The reason for this may be simply that even when the defects were produced during the grinding, they tended to be annealed out of the lattice at 390° C before the catalytic measurements were made. It is noted that this temperature is higher than the Tamman temperature of KBr (about 300° C), at which diffusion of atoms becomes appreciable.



Dehydrochlorination of t-butyl chloride on KBr at an initial pressure of 90 Torr and at three temperatures (○: first run, •: second run)

Table 1 Changes in surface area and catalytic activity (initial rate) with time of grinding (reaction temperature 135°C)

Grinding time (min)	5	10	20
Catalytic activity $(mol \cdot min^{-1} \cdot g^{-1}) \cdot 10^6$	1.9	2.5	2.3
Surface area $(m^2 \cdot g^{-1})$	0.19	0.22	0.25
Specific activity $(mol \cdot min^{-1} \cdot m^{-2}) \cdot 10^6$	10	11	9

For catalytic eliminations, previous studies indicated first order kinetics with respect to the reactant in the range where the backward reaction is neglected [1-3]. In this study, however, the kinetic data appeared to be best explained by an equation derived from the Langmuir isotherm. The reactions occurring on the surface may be written as follows:

 $(CH_3)_3CCl(a) \rightarrow (CH_3)_2C:CH_2(g) + HCl(a)$ (II)

$$HCl(a) \rightarrow HCl(g)$$
 (III)

where the symbols (g) and (a) refer to gaseous and adsorbed species. If the reaction (II) is a rate-determining process, the following rate equation is given: r = k K p/(1 + K p), (K is the equilibrium constant of reaction (I), k is the rate constant of reaction (II), and p is the pressure of reactant). This equation can be tested by the reciprocal equation, $1/r_0 = (1/k) + (1/kKp_0)$, where r_0 and p_0 respectively refer to the initial rate and the initial pressure. Fig. 2 shows that plots of $1/r_0$ as a function of $1/p_0$ are linear at these reaction temperatures. From the temperature dependence of k and K, the activation energy for the decomposition of the intermediate, E, is found to be 96 kJ/



Plots of $1/r_0$ vs. $1/p_0$ for reactions on KBr at three temperatures



Fig. 3

Dehydrochlorination of t-butyl chloride on KBr treated with Br_2 vapor (100 Torr) at 300°C for 1 hr (reaction conditions are the same as those in Fig. 1)

mol, whereas the heat of adsorption of the reactant, q, is -38 kJ/mol.

Fig. 3 shows the reactions on a Br-treated catalyst. It is seen that the reaction rates were markedly increased in comparison with the data in Fig. 1 and that the reproducibility of the data was good for repeated runs, suggesting that the active sites produced by the treatment were stable during the reaction. The plots of $1/r_0$ vs. $1/p_0$ are shown in Fig. 4. The derived *E* and *q* were 159 and -46 kJ/mol, respectively. The increase in *E* appears to be associated with some change in the surface produced by the treatment. It seems likely that the increased catalytic activity must be attributed to the increase in the number of special active sites, since the surface area is not altered by the treatment. With the same catalyst, after various treatments, simultaneous changes in the activation energy and the pre-exponential factor have been found in many cases of heterogeneous catalytic reactions [14].



Plots of $1/r_0$ vs. $1/p_0$ for reactions on Br-treated KBr

Fig. 5 shows a typical solution spectrum of the Br-treated sample. The peak wavelength is strikingly similar to that of additively colored single crystal observed by Mollwo [15]. This band may be ascribed to the formation of V-centers.

Fig. 6 shows typical changes in the catalytic activity, r_0 , and the absorbance at 265 nm as a function of the annealing temperature for the Br-treated specimen. The annealing of the specimen was carried out in the reactor in vacuo for 1 hr at different temperatures. The point marked (a) in the figure represents the activity of the specimen before the treatment. The loss of activity was parallel with the thermal bleaching of the V-centers.

It was also suggested by Teegarden [17] that the V-centers in an alkali halide can be formed independently of the species of halogen used. It seems probable that this situation prevails for a system of KBr + Cl₂ as well as of KBr + Br₂. Therefore, an attempt was made to examine the catalytic properties of Cl-treated KBr. The catalytic activity as a function of the composition of the catalyst is shown in Fig. 7. The activity increases with x and reaches a constant value. The values of x in KBr_{1-x}Cl_x were determined at a temperature of 150°C by gravimetry on the assumption that the treatment may be written as KBr + Cl₂ = KCl + BrCl [18]. Changes in the surface area due to this treatment were negligibly small. In addition, this

Fig. 5 Absorption spectrum of Br-treated KBr dissolved in water

Wavelength/nm

300

265 nm

Br₂/KBr

400

0.4

0.3

0.2

0

400

8

Absorbance,



300

200

Annealing temp./°C Fig. 6

above 250°C. Fig. 8 shows the solution spectrum of the Cl-treated sample. The

absorption band is attributed to the formation of polyhalide ions in the sample.

Discussion

The above findings lead to conclusion that the presence of V-centers in alkali halides contributes to their catalytic activity. In the present case, it should be noted that the specimen was treated under a pressure of Br₂ lower and at a temperature lower than in Mollwo's experiment [15]. Previous studies of additive coloring indicated that the V-center bands are considerably more intense in powder samples or thin films than in single crystals [12, 16, 17]. It is possible that imperfections in crystal are responsible for the formation of the centers and that the surface layer is highly active



Fig. 7 Change in r_0 with composition of Cl-treated KBr (reaction temperature 150°C)



Absorption spectrum of Cl-treated KBr dissolved in water

for the sorption of halogen gas (structure sensitive), although there is a paucity of experimental evidence at present.

In view of the previous results [8], it is now particularly interesting that both the V- and F-centers may contribute to increasing the catalytic activity for the elimination reaction. It has been proposed that elimination reactions on polar catalysts take place due to the formation of polarized complexes given in Fig. 9. Based upon this mechanism, it is

0,5

0,4

0.3

0.1

0

200

Absorbance, log lo/I 0.2

5

4

3

2

1

0

(a)0

100

ro / Torr·min⁻¹



Scheme of elimination reactions on polar catalysts

easy to consider as follows: The V- and F-centers are respectively responsible for the formation of the complexes, $[-X(a) \cdots V$ -center] and $[-H(a) \cdots F$ -center], in the transition state. Although we have no knowledge of physical nature of surface color centers and of the adsorption state of the reactant at present, it is believed that the color centers in alkali halides play an important role in governing the elimination reaction and that their catalytic properties are in some respects similar to those of metal oxide semiconductors which have been investigated by various authors [19].

The authors wish to express their gratitude to Miss. Junko Hiraiwa for valuable assistance in the experiments.

References

 H. Noller and W. Klading, in: "Catalysis Reviews, Science and Engineering", eds. H. Heinemann and J. J. Carberry, Vol. 13, p. 149, Marcel Dekker, New York and Basel 1976.

- [2] G. Simkovich and C. Wagner, J. Catal. 1, 521 (1962).
- [3] K. Hauffe and F. Sitabkhan, J. Catal. 8, 340 (1967).
- [4] H. U. D. Wiesendanger, J. Catal. 7, 283 (1967).
- [5] H. Weise and B. J. Wood, J. Phys. Chem. 71, 4517 (1967).
- [6] J. W. Hall and H. F. Rase, Ind. Eng. Chem. Fundam. 3, 158 (1964).
- [7] a) L. G. Harrison and C. F. Ng, Trans. Faraday Soc. 67, 1787, 1801, 1810 (1971); b) C. F. Ng and K. S. Leung, J. Catal. 67, 410 (1981); 78, 51 (1982).
- [8] S. Kishimoto, W. Ueda, and N. Yoshida, React. Kinet. Catal. Lett. 13, 39 (1980).
- [9] N. N. Greenwood, "Ionic Crystals Lattice Defects and Nonstoichiometry", Butterworths, London 1968.
- [10] L. G. Harrison, in: "Comprehensive Chemical Kinetics", eds. C. H. Bamford and C. F. H. Tipper, Vol. 2, p. 445, Elsevier, Amsterdam 1969.
- [11] T. Takaishi and M. Saito, J. Phys. Chem. 71, 453 (1967).
- [12] H. N. Hersh, J. Chem. Phys. 27, 1330 (1957).
- [13] V. R. Schrader and C. Balarew, Z. Anorg. Allg. Chem. 376, 156 (1970).
- [14] a) E. Cremer, Adv. Catal. 7, 75 (1955); b) A. K. Galwey, Adv. Catal. 26, 247 (1977).
- [15] E. Mollwo, Ann. Phys. 29, 394 (1937).
- [16] A. Glasner and L. Ben-Dor, J. Chem. Phys. 36, 2815 (1962).
- [17] K. J. Teegarden, J. Chem. Phys. 24, 161 (1956).
- [18] J. A. Morrison and K. Nakayama, Trans. Faraday Soc. 59, 2560 (1963).
- [19] J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", p. 241, Academic Press, London and New York 1967.

(Eingegangen am 9. November 1984, E 5852 endgültige Fassung am 12. März 1985)

Dielectric Properties of Polyelectrolyte Solutions Behaviour of Aqueous Solutions of Carboxymethylcellulose with Different Univalent Counterions

F. Bordi and C. Cametti

Dipartimento di Fisica, Università di Roma "La Sapienza", Rome, Italy

Dielectrics / Electrical Properties / Polyelectrolyte / Polymers / Solutions

The dielectric properties of carboxymethylcellulose in various uni-univalent electrolyte solutions in the frequency range from 1 KHz to 10 MHz have been measured by means of a conventional impedance bridge technique. — Two contiguous dielectric dispersions, due to different molecular mechanisms, have been observed, in accordance with the usual behaviour of linear, high-charged polyelectrolytes. — The influence of the molecular weight, polyion concentration and different monovalent counterions (Na⁺, K⁺, Li⁺) has been examinated. — The results are analyzed in terms of rod-like polyelectrolyte dielectric models taking into account the polarization due to the fluctuation in the counterion concentration.

Introduction

Considerable interest has been recently developed to the dielectric properties of rigid-rod-like polymers both because many biological substances possess this structure and because a number of theoretical studies deals with this defined geometrical systems, rather than flexible polymers, thus making quantitative comparison possible.

The phenomenologic feature usually displayed by polyelectrolyte aqueous solutions consists of two adjacent dispersion regions in the frequency interval between 0.1 to 10^4 kHz, besides the dipolar relaxation region of the aqueous phase which occurs at microwave frequencies. The low-frequency dispersion may be very large and it is due to the displacement of loosely bound counterions. The mean relaxation time and the dielectric increment are molecular weight dependent.

The high-frequency relaxation process is attributed to a Maxwell-Wagner type process caused by differences in the ionic conductivities of the polymer domain and bulk medium, or, in some cases, to a radial diffusion of counterions.

Generally, the parameters of this dispersion are molecular weight independent.

All parameters show, however, dependence on polyelectrolyte concentration and on the concentration of added salt.

Ber. Bunsenges. Phys. Chem. 89, 747-754 (1985) - © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1985. 0005-9021/85/0707-0747 \$ 02.50/0