was isolated in 48% yield while 65% dimethyl sulfide was recovered from the oxidation of benzyl alcohol described above in the representative procedure of oxidation. These results support the assignment of dimethyl sulfoxide as the oxidant; however, in the absence of oxygen the reaction failed (only 3% benzaldehyde was formed). In a second experiment under oxygen-free conditions *t*-butyl peroxide (0.001 mole) was added to a solution of benzyl alcohol (0.010 mole) and dimethyl sulfoxide (0.070 mole) at 190° and a second portion of *t*-butyl peroxide (0.001 mole) was added 2 hr. later. After a total reaction time of 4 hr., the reaction mixture was processed and gave benzaldehyde in 60% yield. These data require the appearance of radicals in the mechanistic scheme of this oxidation. In addition, experimental conditions qualitatively suggest that electron-releasing substituents *para* to the carbinol carbon enhance reaction while electron-withdrawing groups retard oxidation. These matters are currently under investigation.

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RECEIVED OCTOBER 25, 1963

On the Problem of Radioactive Radiation of Sulfur-35 Influencing the Catalytic Dehydration of Cyclohexanol

Sir:

In 1958, the authors reported that introduction of radioactive sulfur-35 increased noticeably the catalytic activity of the mixed catalyst, $MgSO_4 + Na_2SO_4$, in the cyclohexanol dehydration reaction.[1] That was the first reported radioactive catalyst. Later this observation was confirmed in the Oak Ridge National Laboratory.[2] Furthermore, we found that external irradiation of a catalyst with electrons of high energy does not give this effect.[3,4] Krohn and Smith[5] came to the same conclusion.

Recently, Krohn and Wymer[6] conducted a detailed investigation of radioactive catalysts. They believe that the increase in activity of such catalysts is due to their greater surface rather than to the radioactive effect. This was also mentioned in earlier reports.[7,8]

The effect of radioactive radiation on the structure and area of the surface of solids has been noted in a number of our publications.[9-12] However, we have succeeded in preparing radioactive and nonradioactive catalysts of the same chemical composition with practically equal specific surfaces. In our first report[1] this was taken for granted when comparing catalytic properties of radioactive with those of nonradioactive catalysts. However, since the specific surface of the catalysts has become a problem of special interest, we present in Table I the results of measurements made by the absorption of krypton. A more detailed report is given elsewhere.[13]

TABLE I

CHARACTERISTICS OF CATALYSTS ($MgSO_4 + Na_2SO_4$) USED IN CYCLOHEXANOL DEHYDRATION

(S^{35} introduced as $Na_2S^*O_4$)

Catalyst no	Na_2SO_4 content, %	Absolute radioactivity, mc./g.	Catalytic activity at 410° %/min. (weight of the catalyst, 0.1 g.)	Specific surface, m.²/g.	Specific catalytic activity, %/m.² min.
1	0	0	23.5	15.52	15.1
2	100	0	2.5	0.71	35.7
3	2.07	0	10.1	5.73	17.7
4	21.87	0	3.5	2.02	17.3
4x	21.87	105.2	9.6	2.08	46.1
5	4.06	0	7.8	11.67	6.1
5x	4.06	9.2	12.6	10.41	12.1
6	0.52	0	12.8	13.27	9.6
6x	0.52	1.26	14.6	5.90	24.7

As Table I shows, the greater the Na_2SO_4 content, the less is the specific surface of a catalyst. Furthermore, the catalytic activity changes although the specific surface remains practically constant, so that contrary to the data of Krohn and Wymer,[6] the specific catalytic activity increases with the increase of radioactivity. The greatest increase of catalytic activity in our experiments was shown by catalyst 4x which had the lowest specific surface (2 m.²/g.) and the highest specific radioactivity (105.2 mc./g.).

Evidently, the conditions which Krohn and Wymer[6] used to prepare their catalyst were in some way unfavorable. This also explains why the values which they report for the activation energy of the cyclohexanol dehydration are different from ours.[1] Our nonradioactive catalysts maintained their activity when stored for more than 500 days while theirs displayed a rather quick and steady drop within several hours. Therefore, these authors had to conduct two series of experiments, one with fresh catalysts and one with catalysts which had already been used for a number of hours.

Figure 1 shows the change in the catalytic activity of our radioactive catalyst 4x upon storage. The lowest curve represents control samples of a nonradioactive catalyst having the same composition as 4x and stored for the same length of time. It clearly follows from these data that the catalytic activity of a nonradioactive mixed catalyst $MgSO_4 + Na_2SO_4$ is maintained even after 1.5 years of storage. Decrease in the catalytic activity of a radioactive catalyst is caused only by the decay of the radioactive isotope introduced into it.

The reasons for the instability of catalysts prepared by Krohn and Wymer should be studied. It is not unlikely that the amount of water on the surface of the catalyst is of importance.

It was shown by Balandin, *et al.*,[14] that the catalytic activity of magnesium sulfate is marked at 360°, but gradually decreases between 280 and 340°. This may probably be attributed to the formation of a hydrate on

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[1] A. A. Balandin, Vict. I. Spitsyn, N. P. Dobrosel'skaya, and I. E. Mikhailenko, *Dokl. Akad. Nauk SSSR*, **121**, 495 (1958).

[2] *Nucl. Sci. Abstr.*, **24A**, 3296 (1960).

[3] A. A. Balandin, Vict. I. Spitsyn, N. P. Dobrosel'skaya, I. E. Mikhailenko, I. V. Vereshchinskyi, and P. Ia. Glasunov, *Isv. Akad. Nauk SSSR Otd. Khim. Nauk*, 565 (1961).

[4] A. Balandin, V. Spitsyn, N. Dobrosselskaia, I. Mikhailenko, I. Verechtchinski, and P. Glazunov., *Actes Congr. Intern. Catalyse 2^e Paris, 1960*, 1415 (1961).

[5] N. A. Krohn and H. A. Smith, *J. Phys. Chem.*, **65**, 1919 (1961).

[6] N. A. Krohn and R. G. Wymer, Paper CN-14/17, presented at the IAEA Conference on the Application of Large Radiation Sources in Industry, Salzburg, Austria, 1963.

[7] H. A. Smith, *Actes Congr. Intern. Catalyse, 2^e, Paris, 1960*, 1427 (1961).

[8] "Fundamental Nuclear Energy Research," a special report of the U. S. AEC (Prepared by Division of Plans and Reports), Dec., 1962, p. 202.

[9] Vict. I. Spitsyn, L. I. Zemlianova, I. E. Mikhailenko, V. V. Gromov, and I. E. Zimakov, *Dokl. Akad. Nauk SSSR*, **139**, 1163 (1961).

[10] L. D. Beliakova, V. V. Gromov, A. V. Kiselev, and Vict. I. Spitsyn, *ibid.*, **138**, 1139 (1961).

[11] Vict. I. Spitsyn and I. E. Mikhailenko, "Proceedings of the 2nd All-union Conference on Radiation Chemistry," USSR Akademy of Science Publishing House, Moscow, p. 642; *Chem. Abstr.*, **58**, 9777*g* (1963).

[12] I. E. Zimakov, N. P. Dobrosel'skaya, and Vict. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **148**, 884 (1963).

[13] A. A. Balandin, Vict. I. Spitsyn, N. P. Dobrosel'skaya, and I. E. Mikhailenko, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, in press.

[14] A. A. Balandin, M. B. Turova-Polak, A. E. Agronomov, N. M. Khorlina, and L. S. Kon'kova, *Dokl. Akad. Nauk SSSR*, **114**, 773 (1957).

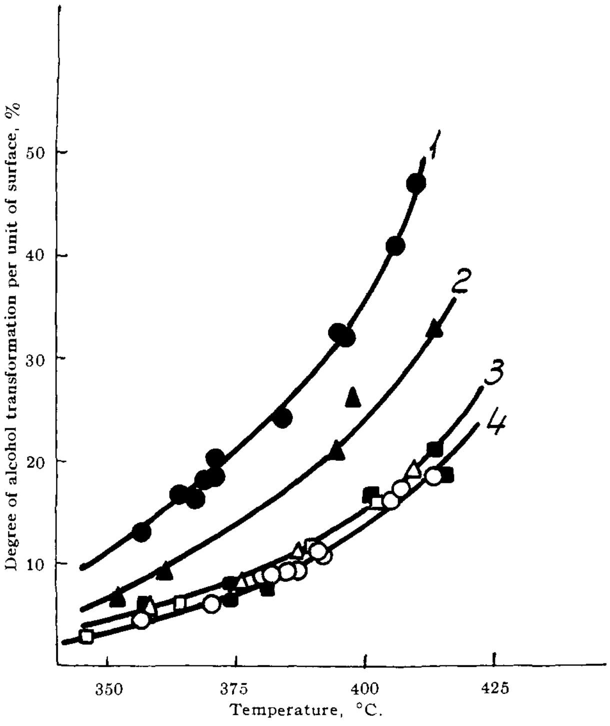

Fig. 1.—Change in the catalytic activity of sample 4x with time (cyclohexanol dehydration reaction). Time of storage: curve 1, 1 day (105.2 mc./g.); curve 2, 315 days (8.5 mc./g.); curve 3, 503 days (1.9 mc./g.); curve 4, a nonradioactive sample stored for the same periods of time (the corresponding points are shown by open dots).

the surface of the crystals. On the other hand, there are reports[15] that preliminary heating of alumosilicate catalysts *in vacuo* increases their catalytic activity in the cracking of cumene, but subsequently their activity drops more quickly than that of the air-dried catalysts which were not vacuum-processed. Krohn and Wymer[1] heated their catalysts *in vacuo* while ours were air-dried.

In conclusion, it should be pointed out that we have also noted[16] a considerable increase in the rate of dehydration of isopropyl alcohol over radioactive tricalcium phosphate which contained isotopes Ca^{45} and P^{32}. There are cases, depending upon the nature of the catalyst and the reaction studied, in which the introduction of radioactive isotopes reduces the catalytic activity.[17] This, however, does not contradict the results obtained by us on cyclohexanol dehydration over the mixed catalyst $MgS^*O_4 + Na_2S^*O_4$.

(15) K. V. Topchieva and E. N. Rosolovskaya, *Neftekhimiya*, **2**, 298 (1962).

(16) Vict. I. Spitsyn, A. A. Balandin, I. E. Mikhailenko, and N. P. Dobrosel'skaya, *Dokl. Akad. Nauk SSSR*, **146**, 1128 (1962).

(17) Vict. I. Spitsyn, I. E. Mikhailenko, and G. N. Pirogova, *ibid.*, **140**, 1090 (1961).

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RECEIVED SEPTEMBER 26, 1963

Specific Interactions of Optically Active Ions as Studied by Conductance

Sir:

The conductances of *d*- and *l*-tris(ethylenediamine)-cobalt(III) iodide ($Co(en)_3I_3$) have been measured at 25° in water and in 0.003 *M* solutions of both *d*- and *l*-sodium tartrate in water. A significant difference in mobility was found between the two cobalt isomers in solutions of optically active tartrates.

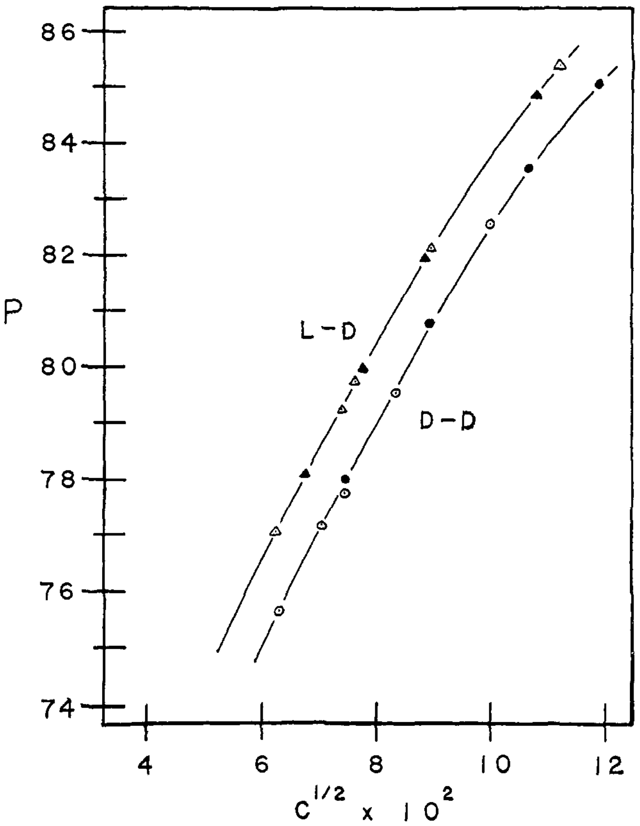

Fig. 1.—A plot of P *vs.* $c^{1/2} \times 10^2$ for the four samples of $Co(en)_3I_3$ in aqueous sodium *d*-tartrate solution. L–D and D–D label, respectively, curves for runs on the *l*-$Co(en)_3I_3$ and *d*-$Co(en)_3I_3$ in aqueous solution of sodium *d*-tartrate. The following symbols denote the four $Co(en)_3I_3$ samples used: △, l_1; ▲, l_2; ⊙, d_1; ●, d_2.

Instrumentation and techniques for conductance measurements made in pure water were similar to previously described methods and apparatus.[1] Conductances of the $Co(en)_3I_3$ isomers were measured in aqueous sodium tartrate by making dilution runs using portions of the same stock solution of sodium tartrate. It was thus possible to vary the concentration of the $Co(en)_3I_3$ without changing the sodium tartrate concentration. The *d*- and *l*-$Co(en)_3I_3$ samples prepared by the method of Dwyer[2] had specific rotations of +89.2° and −89.7°, respectively. Dwyer[3] reported $[\alpha]_D$ +89° and −90° for the two isomers. To assure removal of traces of ionic impurities, the salts were carefully recrystallized three times from hot 50% ethanol–water solutions which had been filtered through sintered glass funnels. Partial racemization which occurred during the latter operation could easily be corrected for in the final calculations. Two samples of salt were prepared and purified. The final rotations were: d_1 ($[\alpha]_D$ +73.5°), d_2 ($[\alpha]_D$ +36.0°), l_1 ($[\alpha]_D$ −79.4°), l_2 ($[\alpha]_D$ −80.1°). Although sample d_2 was significantly racemized, it was run as a check on our method of correction for racemization. For conductance runs these slightly hygroscopic salts were dried to constant weight at 100° at 0.001 mm. and weighed on a microbalance in an air-tight weighing ampoule. Sodium *d*-tartrate (Powers-Weightman-Rosengarten Co., Analytical Chemicals, Philadelphia, Pa.) and sodium *l*-tartrate (Aldrich Chemical Co., Inc., Milwaukee, Wis.) were used without further purification.

(1) J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961), R. W. Kunze and R. M. Fuoss, *ibid.*, **66**, 930 (1962).

(2) J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Syn.*, **6**, 183 (1960).

(3) J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *ibid.*, **6**, 185 (1960).