10, Fig. 2) that the circular dichroism is zero near the absorption maximum at 252 mμ and has a maximum and minimum at wave lengths where the absorption is about 60% of its maximum. The circular dichroism curve is not symmetric as predicted for an isolated absorption band, but the spectrum shows an overlapping of the 200 mμ band. We therefore propose that the measured circular dichroism is caused by a perpendicularly polarized absorption band in poly A centered at 250 mμ. It follows that the positive lobe of this circular dichroism curve is not primarily caused by an $n \rightarrow \pi^*$ transition at 262 mμ. A calculation of the sign of the circular dichroism curve for poly A[11] gives results in agreement with experiment and thus further supports our interpretation.

The poly U data are analogous to poly A and presumably have the same explanation. The poly C circular dichroism curve shows a single peak, but as the poly C spectrum is more complicated and the poly C geometry is not known, no interpretation can be given at this time.

DNA should show the behavior given in Fig. 1. The circular dichroism maximum and minimum[12] and ORD trough and two peaks[13] are in good agreement with those calculated from the DNA spectrum.

Polypeptide helices also show the type of circular dichroism and ORD curves given in Fig. 1. However, these helices have the complication of normal circular dichroism curves also being present in the same wave length region. The amide transition moments are tilted with respect to the helix axis instead of being essentially either parallel or perpendicular to it as in DNA-like helices. This leads to normal circular dichroism curves at the absorption maxima of the parallel and perpendicular components of the tilted transition moments. Furthermore, there is apparently a contribution from the amide carbonyl $n \rightarrow \pi^*$ transition.[14,15] Calculation of the sum of these effects leads to satisfactory agreement with experiment.[16]

In summary all single or multistranded helices with an absorption band polarized perpendicular to the helix axis should show the effect given in Fig. 1. However, the effect can be easily resolved only for an isolated band. Therefore, helical dye arrays would seem to provide the best example. One can also orient the helices and measure the rotation or circular dichroism for light incident parallel to the helix axis; only perpendicularly polarized transitions will contribute.

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The Selective Oxidation of Arylcarbinols to Aldehydes[1]

Sir:

Recently, Pfitzner and Moffatt[2] have reported that the oxidation of alcohols in the presence of phosphoric acid, dicyclohexylcarbodiimide, and dimethyl sulfoxide produced aldehydes and ketones. This reaction appears to involve dimethyl sulfoxide as a reactant and resembles an earlier report by Kornblum[3] and Nace and Monagle,[4] who obtained aldehydes from the reaction of primary halides or tosylates with dimethyl sulfoxide.

In continuation of our study of the reactions of alcohols in dimethyl sulfoxide,[5] we wish to report the selective oxidation of a variety of benzyl alcohols to the corresponding aldehydes. This oxidation proceeded conveniently by refluxing the alcohol in dimethyl sulfoxide and was facilitated by passing a stream of air through the reaction medium. The reaction stopped at the aldehyde stage with over-oxidation to the acid occurring in only one case in 3% yield. In fact, when a solution of benzaldehyde in dimethyl sulfoxide was refluxed (190°) for 24 hr. with air passing through the solution, only 1.6% benzoic acid was isolated with 87% benzaldehyde recovered. The unique feature of these observations is the role of dimethyl sulfoxide in inhibiting further oxidation of aldehydes yet permitting the oxidation of alcohols.

The following procedure is representative of this oxidation. A solution of benzyl alcohol (10.8 g., 0.10 mole) and dimethyl sulfoxide (54.6 g., 0.70 mole) was heated for 14 hr. at reflux with air passing through the solution. The mixture was cooled, diluted with water, extracted with ether, and the ether extract washed with water, dried, and distilled. The yield of pure benzaldehyde, b.p. 75–77° (22 mm.), $n^{20}D$ 1.5440, 2,4-dinitrophenylhydrazone m.p. 236–237°, was 8.5 g. (80%). Table I contains a variety of examples which were subjected to these conditions for 4 to 48 hr. Unless stated otherwise, the yields in Table I represent isolated purified material.

TABLE I

OXIDATION OF BENZYL ALCOHOLS TO ALDEHYDES

Alcohol	Product	% yield
p-NO_2–$C_6H_4CH_2OH$	p-NO_2–C_6H_4CHO	77[a]
m-NO_2–$C_6H_4CH_2OH$	m-NO_2–C_6H_4CHO	63[b]
o-NO_2–$C_6H_4CH_2OH$	o-NO_2–C_6H_4CHO	27[c]
p-Cl–$C_6H_4CH_2OH$	p-Cl–C_6H_4CHO	86
o-Cl–$C_6H_4CH_2OH$	o-Cl–C_6H_4CHO	78
$C_6H_5CH_2OH$	C_6H_5CHO	80
p-$CH_3C_6H_4CH_2OH$	p-CH_3–C_6H_4CHO	85
p-CH_3O-$C_6H_4CH_2OH$	p-CH_3O–C_6H_4CHO	8.8
	$(p\text{-}CH_3O\text{-}C_6H_4CH_2\text{–})_2\text{–}O$	85
$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	60[d]
$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CHO$	26
	O ‖	
$C_6H_5CH_2CHOHCH_3$	$C_6H_5CH_2CCH_3$	25[d]
	$C_6H_5CH{=}CHCH_3$	36[d]

[a] Crude yield of 90%. [b] An additional 13.5% of the aldehyde was isolated as the 2,4-dinitrophenylhydrazone. [c] This was isolated as the 2,4-dinitrophenylhydrazone. [d] These yields were determined by vapor phase chromatography.

Although air facilitates the reaction, oxygen does not appear to be the oxidant. There was no oxygen uptake when the oxidation of benzyl alcohol was performed over a measured volume of oxygen under conditions which produced benzaldehyde in 60% yield. In this experiment dimethyl sulfide, identified by the mercuric chloride derivative, m.p. 146–148° (lit.[6] m.p. 150–151°),

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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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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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