

A Note on the Cannizzaro Reaction.

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In the course of the investigation on the effect of oxygen and ferromagnetic metals on the addition of hydrogen bromide to allyl bromide, the authors⁽¹⁾ came to suspect that the effect of peroxides on the Cannizzaro reaction observed by M. S. Kharasch and M. Foy⁽²⁾ was really caused by molecular oxygen, because molecular oxygen was found the active catalyst influencing the direction of addition and the yield of the products in the reaction of hydrogen bromide with allyl bromide although the experimental evidence so far obtained could not totally exclude the possibility that peroxides were active also as such.⁽³⁾ But the authors'

Series of experiment	No. of exp.	Added	Extent of Cannizzaro reaction (%)
I Peroxide-free benzaldehyde	1	None	10
	2	None	9
	3	Hydroquinone, 0.1 g.	8
II Purified benzaldehyde, exposed to air for 5 minutes	4	None	53
III Commercial benzaldehyde	5*	None	76
	6	None	83
IV Peroxide-free benzaldehyde	7	Reduced iron, 1.5 g.	10
	8	Reduced nickel, 1.5 g.	11
	9	Reduced nickel, 1.5 g. Hydroquinone, 0.1 g.	9
	10	Reduced nickel, 1.5 g. Hydroquinone, 0.1 g.	10

* Reaction time: 2 hours.

(1) This Bulletin, **12** (1937), 54.

(2) *J. Am. Chem. Soc.*, **57** (1935), 1510.

(3) This Bulletin, **11** (1936), 798; **12** (1937), 133, 173.

expectation has not been proved, and the Cannizzaro reaction may be more reasonably regarded as a chain reaction in which the peroxide of the aldehyde concerned, even though present in very minute traces, plays an important part. A support to such an interpretation is given by the fact that benzaldehyde has been found extremely sensitive to peroxide formation even in the dark,⁽⁴⁾ and that the Cannizzaro reaction does not undergo even the slightest influence of ferro-magnetic metals, which cause an effect quite similar to that of oxygen, in the addition of hydrogen bromide to allyl bromide. The experimental results are summarised in the accompanying table. Benzaldehyde (10 c.c.) was shaken with an excess of aqueous potassium hydroxide (13.8 N, 10 c.c.) in vacuum in the dark at room temperature for three hours, and the extent of Cannizzaro reaction was determined from the alkali consumed.

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(4) Allyl bromide does not form peroxide in the dark, this Bulletin, **11** (1936), 798.