

Note on Bimolecular Reactions.—In homogeneous bimolecular reactions, integration of the two velocity expressions, $dx/dt = k(a - x)^2$, when the two reacting molecules are alike or of the same initial concentrations, and $dx/dt = k(a - x)(b - x)$, when the reacting molecules are unlike, leads to the following familiar equations

$$k = \frac{1}{ta} \times \frac{x}{(a - x)}, \text{ and} \quad (1)$$

$$k = \frac{1}{t(a - b)} \times \log \frac{b(a - x)}{a(b - x)} \quad (2)$$

where the symbols have their usual significance. It is a physical necessity that expression (2) reduce to (1) if $b = a$. Yet it is obvious that (2) assumes the form $0/0$ when $b = a$.

It has been shown in several places¹ that (2) does become equal to (1) under this condition, by expanding the logarithm term in (2) in series and evaluating the resulting expression. However, the methods quoted require a page or more of mathematical simplification to obtain the desired result. On the other hand, making use of the customary way of evaluating $0/0$, we have been able to find in a very simple manner the limiting value of the ratio as $b \rightarrow a$, and from this to show the identity of the two expressions. It proves to be a rather interesting situation, and since it does not appear in any of the ordinary textbooks on the subject, we thought that it might be worth while to pass it on.

From (2)

$$k = \frac{\log b + \log(a - x) - \log a - \log(b - x)}{t(a - b)} = \frac{0}{0}$$

when $b = a$. Now since this would be $0/0$ for all finite values of x and t , for our purpose we may treat these as constants and take

$$\lim_{b \rightarrow a} \frac{f(b)}{F(b)}$$

Treating b as the variable, and differentiating numerator and denominator separately² we get³

$$\frac{\frac{1}{b} - \frac{1}{b-x}}{-t}$$

¹ See, for example, Nernst and Schönfiess, "Einführung in die mathematische Behandlung der Naturwissenschaften," Oldenbourg, Munich, 1923, p. 262 *et seq.*; Taylor, "Treatise on Physical Chemistry," D. van Nostrand Company, New York, 1925, p. 869.

² See any standard calculus book for explanation of rule to evaluate $0/0$, such as Wilson, "Advanced Calculus," Ginn and Co., 1921, p. 61, or Love, "Calculus," The Macmillan Company, 1921, p. 204.

³ Although b was constant in the original differential equation, we are considering here the special case when $b \rightarrow a$, that is, variation in b 's value.

and on simplifying = $x/tb(b - x)$. This, of course, when $b = a$, becomes $x/ta(a - x)$, which is expression (1).

CONTRIBUTION FROM THE
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RECEIVED JULY 22, 1930
PUBLISHED OCTOBER 6, 1930

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE SKRAUP REACTION WITH CERTAIN AZO COMPOUNDS

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RECEIVED FEBRUARY 27, 1930

PUBLISHED OCTOBER 6, 1930

In the course of an investigation of the possible explanation of the reaction mechanism of the formation of *p*-phenanthroline in the Skraup reaction with *p*-aminoresorcin dimethyl ether, *p*-benzene-azo-resorcin dimethyl ether was subjected to the Skraup reaction and the product was found unexpectedly to be also *p*-phenanthroline; the yield in this case was three times as good as in the same reaction with *p*-aminoresorcin dimethyl ether. The formation of *p*-phenanthroline was also established, in the same way, from *p*-benzene-azo-resorcin, whereas from *p*-aminoresorcin, no crystalline matter could be isolated, on working under the same conditions.

From these facts it seemed that in case of the Skraup reaction with rather unstable amines, better results might follow if the corresponding azo compounds were used as reactants, and here I have extended this study to several azo compounds.

Concerning the study of the Skraup reaction with azo compounds, work has been reported by Claus and Stegelitz¹ and later by Lellmann and Lippert.² They established the formation of the corresponding ring compounds in this reaction, but the yield in each case was reported to be very poor. In the present investigation the reactions were carried out with the addition of arsenic acid, this being the only difference from the methods of previous investigations.

TABLE I

EFFECT OF ARSENIC ACID IN THE SKRAUP REACTION WITH AZO COMPOUNDS

Reactants	Products	Yield, g.	
		Presence of H ₂ AsO ₄	Absence of H ₂ AsO ₄
Azobenzene, 10 g.	Quinoline picrate	0.5	0.55
	6,6'-DiquinolyI	5.7	1.2
<i>p</i> -Benzene-azo-resorcin dimethyl ether	Quinoline	2.0-2.5	1.4
	<i>p</i> -Phenanthroline	1.35-1.5	0.3

¹ Claus and Stegelitz, *Ber.*, 17, 2380 (1884).

² Lellmann and Lippert, *ibid.*, 24, 2623 (1891).