cated the importance of an alkaline medium in the transformation.[3] The reaction rate study conducted by Westheimer[4] indicated the existence of a bimolecular reaction between benzil and hydroxyl ion which can best be explained by the formation of the same negative ion. Recent investigation by

(3) Ingold, "Ann. Repts. Chem. Soc., (London)" Vol. XXX, 1933, p. 177.

(4) Westheimer, THIS JOURNAL, **58**, 2209 (1936).

Roberts and Urey[5] on the oxygen interchange of benzil with water of a higher concentration of H_2O^{18} indicates a more rapid exchange in alkaline than in neutral solution which is explained by the rapid, reversible addition of hydroxyl ion to form a negative ion with benzil, followed by rearrangement.

(5) Roberts and Urey, *ibid.*, **60**, 880 (1938).

STATE COLLEGE, PENNA. RECEIVED JUNE 4, 1938

COMMUNICATIONS TO THE EDITOR

THE SALT EFFECT IN THE PARAMAGNETIC CONVERSION OF p-HYDROGEN

Sir:

In 1934 Sachsse [*Z. physik. Chem.*, **B34**, 429 (1934); *Z. Elektrochem.*, **40**, 531 (1934)] reported that the rate constants for the conversion of p-hydrogen by solutions of paramagnetic ions were independent of the concentrations of these ions if the change in solubility of hydrogen with changing ionic strength were taken into account. To this is now added the fact that these rate constants are also independent of the concentration of added diamagnetic salts. The measurements were made by shaking the solutions with p-H_2 at a shaking speed in the range at which the conversion rate was independent of the shaker speed. The ratio of gas volume to solution volume was known and kept constant. The apparent rate was independent of hydrogen pressure.

Some representative data are given in the following table for which the solution volume is always 100 cc., the gas pressure *ca.* 100 mm., the concentration of manganous chloride 0.02 M, at room temperature.

Expt.	Molality of diamagnetic salt	$k'_{0.02} \times 10^3$	l(Ostwald)	$k(l, m^{-1},$ $min.^{-1})$
1	0	3.03	0.0198	7.9
2	0.3 M CaCl$_2$	2.75	.0173	8.2
3	0	2.15	.0198	8.0
4	1 M NaNO$_3$	1.65	.0158	7.7
5	2 M NaNO$_4$	1.41	.0127	8.2
6	0.6 M BaCl$_2$	1.56	.0151	7.7

In experiments 1 and 2 the gas volume is 45.1 cc.; in expts. 3 to 6 the gas volume is 64 cc. k' is the observed first order rate constant calculated by $k'_{0.02} = \frac{1}{t} \log \frac{(p\text{-}H_2)_0}{(p\text{-}H_2)_t} - k'_w$ where t is the time in minutes, $(p\text{-}H_2)_0/(p\text{-}H_2)_t$ is the rate of the initial

p-H_2 concentration to that at the time t and k'_w is the correction for the conversion by pure water under the same conditions and calculated in the same way. For expts. 1 and 2 $k'_w = 0.07 \times 10^{-3}$ and for expts. 3 to 6 $k'_w = 0.05 \times 10^{-3}$. k is the velocity constant reduced to unit Mn^{++} ion concentration and corrected for the gas not in solution by the relation $k = \frac{V_g \times 2.303}{V_s \times l \times M_{MnCl_2}} \times k'$ where V_g is the gas volume, V_s the solution volume, l the Ostwald solubility of H_2 (from Seidell's "Solubilities") and M_{MnCl_2} the molality of the manganous chloride.

Thus the rate of conversion of p-$H_2 \longrightarrow o$-H_2 by Mn^{++} can be expressed by

$$\frac{-d(p\text{-}H_2)}{dt} = k(Mn^{++})(p\text{-}H_2)$$

where (Mn^{++}) and $(p\text{-}H_2)$ are the concentrations of Mn^{++} ion and p-H_2, respectively. There is no need to introduce any activity factor of Brönsted $f_{Mn^{++}}f_{H_2}/f_{Mn^{++}\cdot H_2}$, although the concentration of the diamagnetic salts was carried as high as 4 M NaNO$_3$ and 2.4 M CaCl$_2$ in 0.02 M manganous chloride. If it is incorporated it must be a constant and this is not unreasonable since the two reactants completely retain their independent identities throughout the reaction.

The effectiveness of the inhomogeneous magnetic field of the ion is independent of the ionic environment of the paramagnetic ion. This is in agreement with the observation of Sachsse that solutions of manganous sulfate and manganous chloride give the same rate constant.

DEPARTMENT OF CHEMISTRY MELVIN CALVIN
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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