Partition Equilibrium of Cumene Hydroperoxide between Water and Cumene[*]

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In the "cumene process", the hydroperoxide (CHP) is sometimes obliged to come in contact with water chiefly because the latter is the general stabilizer to thermal decomposition of CHP in the oxidate. The contact is operated during and after the hydroperoxidation, where dissolution of CHP in the water phase cannot be neglected. In this relation, studies on the partition equilibrium of CHP between water and cumene seem to contribute to the solution of the problem, so the partition constant K and its dependence on the temperature and CHP concentration were investigated. We can find no description of such an investigation in the literature up to the present, though CHP is said to be insoluble in water[1].

Experimental

Apparatus and Sample.—Thermostat adjusted to ±1°C, and conical flasks of 200 cc. and 500 cc. with tight stoppers were used.

Cumene was prepared by alkylation of benzene with propylene in the presence of 90% sulfuric acid at 20～30°C. The fraction of the mixture after washing with concentrated sulfuric acid and 25% aqueous sodium hydroxide for more than 10 times, had b. p. 151～3°C.

CHP was prepared by the liquid phase oxidation of the cumene with oxygen gas at 128～132°C. The sodium salt was precipitated by shaking the steam-stripped oxidate with 25% aqueous sodium hydroxide, filtering off, washing with petroleum benzine, and dissolving in water. The solution was acidified with carbon dioxide, the oily layer extracted with petroleum ether, dried over anhydrous sodium sulfate, filtered and concentrated at 50～70°C under 1～3 mmHg pressure. The clear residue was found to contain 99% be weight of CHP by iodometry.

Method.—Several solutions, varying in concentration of CHP in the cumene were prepared in the flasks. Distilled water was added to the same volume as that of the oil and they were settled for a certain time after being subjected to vigorous shakings every 10～15 min. Volumes of samples employed for analysis were 1 or 5 cc. for the oily layer and 20 or 25 cc. for the aqueous layer according to the concentration of CHP in solution.

Each group of four samples was brought side by side in the thermostat for 2.5 hr. at 10, 20, 35, 50°C, and served for analysis.

Determination of Partition Constants.—We assume that v_1 is the volume (cc) of N/10 aqueous sodium thiosulfate consumed for 5 cc. of oily layer, v_2 that for 25 cc. of water, and c_1, c_2 moles of CHP per litre in the oily and aqueous layer respectively. Then the partition constant $K(t)$ at t°C is shown as follows.

$$K = c_2/c_1 = 0.2\, v_2/v_1$$

Results are given in Table I.

TABLE I

PARTITION CONSTANTS AT SEVERAL TEMPERATURES

t (± 1°C)	v_1 (cc.)	v_2 (cc.)	K ($\times 10^2$)
10	9.46	1.75	3.7
	9.56	1.82	3.8
	19.70	3.12	3.2
	36.20	6.38	3.5
20	4.30	0.64	3.0
	9.10	1.48	3.3
	19.18	2.48	2.6
	32.45	4.00	2.5
35	5.40	0.62	2.3
	11.43	1.28	2.2
	23.03	2.32	2.0
	44.68	4.50	2.0
50	6.10	0.51	1.7
	11.40	1.10	1.9
	21.76	2.05	1.9
	39.73	3.37	1.7

The Time Required for the Equilibrium.—Some samples in Table I were further taken to determine K under the settling time of 1.5 hr., which however gave approximately the same value, as in the case of Table I. The following data show the variation of CHP concentration with the settling time. In these cases the temperature was subjected to the fluctuation ranging from 7 to 15°C and the shaking time of 10～15 min. was not exactly maintained.

A and B in Table II are the volume (cc.) of thiosulfate solution required for titrating 5 cc. of aqueous layer of the system, composed of 200 cc. of distilled water and 200 cc. of 15～20% CHP solution, prepared from pure CHP and the steam-stripped oxidate of cumene respectively.

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1) H. Hock and S. Lang, *Ber.*, 77, 259 (1944).

TABLE II

VARIATION OF CHP CONCENTRATION IN THE AQUEOUS LAYER WITH TIME AS EXPRESSED BY CC. OF THIOSULFATE SOLUTION

	10 min.	2 hr.	4 hr.	6 hr.	1 week
A	0.54	0.92	0.59	0.56	0.69
B	0.52	0.74	0.39	0.59	0.65

Data for the Practical Oxidate.—A similar method was applied for the practical oxidate of cumene prepared as mentioned above. Results are given in Table III.

TABLE III

PARTITION CONSTANT FOR THE PRACTICAL OXIDATE AT 10°C

v_1'	v_2'	K ($\times 10^2$)
6.18	1.25	1.0_1
12.70	2.41	0.9_5
24.40	4.75	0.9_7

v_1', v_2' are volumes for 1 cc. and 20 cc.

$K=0.05\,v_2'/v_1'$

Discussion

Concentration and Temperature Dependence of Equilibrium Constant K.— Constancy of K regardless of the change of CHP concentration at each temperature seems to be affirmed within the limits of experimental error, while its dependence on the temperature is shown in Table IV and Fig. 1.

TABLE IV

ARITHMETIC MEAN OF CONSTANT, $\overline{K}$ AT EACH TEMPERATURE

t (± 1°C)	$\overline{K}$ ($\times 10^2$)
10	3.6
20	2.9
35	2.1
50	1.8

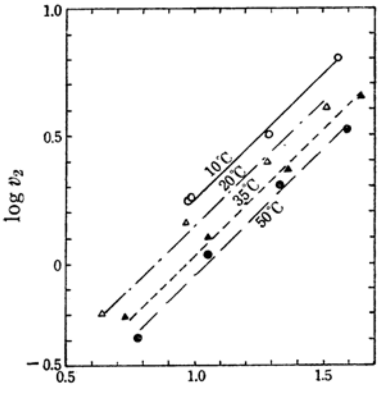

Fig. 1. Relation between log v_1 and log v_2.

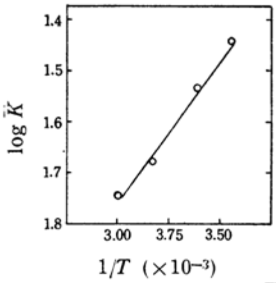

Fig. 2. Relation between log $\overline{K}$ and $1/T$.

Linear relation between log $\overline{K}$ and reciprocal of absolute temperature shown in Fig. 2. suggests that it will satisfy the following thermodynamic formula,

$$\ln K_2/K_1=-Q/R\cdot(1/T_1-1/T_2),$$

where, R is the gas constant, and Q, the heat of transference of 1 mol. of CHP from cumene solution into water under the equilibrium condition. Thus, Q was determined as 3.16 kcal./mol. Accordingly, equilibrium constant K approximately satisfied the following formula,

$$K=1.3_4\times 10^{-4}e^{1580/T}$$

Other Problems.—From data in Table II the equilibrium is supposed to be established within two hours under these conditions. Further, values of K for the practical oxidate appear remarkably smaller than those for pure CHP series. A similar tendency was also observed in other practical cases which may presumably be explained as the influence due to the side products of the hydroperoxidation.

Summary

The partition equilibrium was investigated in relation to the steam-blowing and stripping, during and after the hydroperoxidation of cumene, and the following results were obtained.

1. Equilibrium constant K does not depend on the concentration of CHP within the limit of experimental error, but it depends on the temperature.
2. The partition constant, K approximately satisfies the following formula,

$$K=1.3_4\times 10^{-4}e^{1580/T}.$$

3. The heat of transference of 1 mol. of cumene hydroperoxide from cumene solution into water under the equilibrium condition, was determined as 3.16 k cal./mol.

This article is a part of the investigations of the cumene process which have been studied by many members of Tōkai Electrode Mfg. Co. The authors are grateful to them and wish to express their thanks to Dr. H. Sobue, professor of Tokyo University, for his valuable suggestions and discussions, to Mr. M. Nomaguchi, the chief of our laboratory for his instructive advice and encouragement, and to the authorities of Tōkai Electrode Mfg. Co. for the publication of this work.

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