JOURNAL OF CATALYSIS 11, 187–194 (1968)

# Reaction Pattern of Vapor-Phase Oxidation of Cumene on Vanadium Oxide

L. ZANDERIGHI, P. SCHWARZ, AND S. CARRÀ

*From the Istituto di Chimica Fisica, Universitá di Milano, Milan, Italy*

Received December 27, 1967; revised April 16, 1968

A series of experimental integral reactor data was obtained under mild conditions, that is at 280°, 300°, and 320°C. The oxidation products were $\alpha,\alpha'$-dimethylphenylcarbinol, $\alpha$-methylstyrene, 2-phenylpropylene oxide, acetophenone, benzoic aldehyde, 2-phenylacrolein, maleic anhydride, and benzoic acid. With the help of the most significant intermediates of the oxidation, a reaction scheme is offered. After having shown that thermal and mass-transfer effects were negligible, a kinetic study was performed. The role of the intermediates 2-phenylacrolein in the reaction mechanism is discussed.

## INTRODUCTION

The oxidation of alkyl aromatic hydrocarbons on vanadium pentoxide is particularly challenging because of the difficulties in the thermal control of the reacting system and in the analytical procedure, due to the high number of different kinds of products. Only by operating under relatively bland conditions is it possible to identify the more significant intermediates and to obtain a sufficiently detailed kinetic scheme.

Cumene, owing to the presence of a tertiary carbon atom, is particularly reactive and therefore apt for a complete kinetic analysis by employing bland oxidation conditions. In the present work cumene has been oxidized with air on $V_2O_5$ at 280°, 300°, and 320°C and the experimental results allowed to build a satisfactory reaction scheme.

Previous research on cumene oxidation (*1*) at 400°C showed that the main reaction products were benzoic acid and maleic anhydride.

## EXPERIMENTAL

**Materials.** Cumene, $\alpha$-methylstyrene, and acetophenone, were pure grade products purified by standard methods.

The catalyst was pure $V_2O_5$. It was obtained from a saturated solution of $NH_4VO_3$ by precipitation with $HNO_3$. The filtrated and washed brown product was extruded and dried; it was then heated in air stream at 500°C for 3 days.

The final catalyst in small yellow rods (diameter 0.7 mm, mean length 8 mm) was highly crystalline, as shown by X-ray analysis.

The surface area, determined by BET method, was 3.5 $m^2/g$. The IR spectra, performed on the powder, revealed the presence of the band of pure $V_2O_5$ (*2*, *3*).

**Equipment.** The equipment employed is shown in Fig. 1. The system is fed with air (A) which is first dried through a potassium hydroxide column (B). The flow rate is then measured with a rotameter (C) and sent into a thermostated presaturator (D); it then passes through the saturator (E) which is kept at a slightly lower temperature. This is measured through a precision thermometer. The stream preheated through a coil, to the reaction temperature, is then fed to the reactor (F). This is thermostated through an external sand fluidized bed, heated by a tubular Pyrex glass oven. The oven and reactor temperatures are measured by two thermocouples connected to a recorder (R). The output stream is heated with two IR lamps (L) which avoid product condensation.

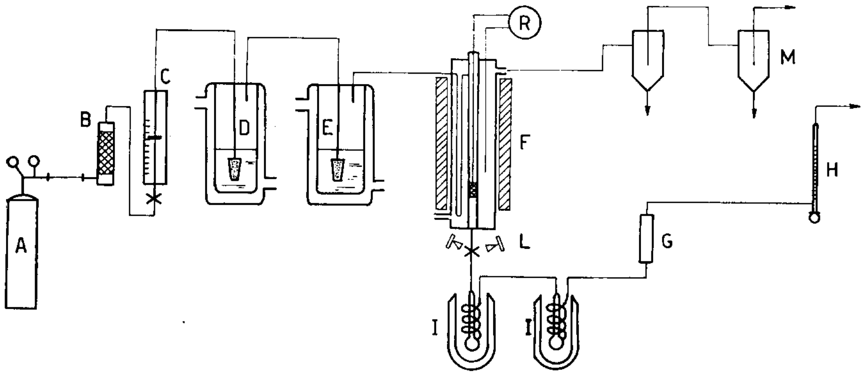


FIG. 1. Apparatus; for the meaning of the symbols, see text.

The products are collected into two weighed traps (I) cooled by a mixture of Dry Ice and acetone. The exit gas flow is then measured with a bubble flow meter (H) after reading its temperature on thermometer (G). M indicates two cyclones employed for dust removal. The reactor is a glass tubular one, with a length of about 30 cm and a diameter 0.8 cm, and its isothermal zone, experimentally determined, is over 10 cm long.

**Procedure.** The reaction was conducted with cumene partial pressures between 8 and 10 mm Hg, corresponding to an $O_2$–cumene ratio of about 16. Once stationary temperature conditions of the saturators and of the reactor had been reached, the feed was started. After about 1 hr, the run was started and the checks of the process variables were systematically effected at fixed time intervals. At the end of a run, that is when about 0.7-1.5 g of cumene had been evaporated, the temperature of the reactor was brought to 400°C and dried air was fed during the night to reestablish the original conditions for the following run. Such a procedure enabled us to obtain experimental data with a good reproducibility. This seems to indicate that the partial reduction of the vanadium ion to a stationary valency between 4 and 5 (*4*) occurs substantially during the conditioning before the run is started.

The amount of cumene evaporated during a run was evaluated from the amount of air fed to the evaporators and from the cumene vapor pressure (*5*). A blank run was performed to verify that the mixture fed to the reactor was saturated.

The contact time was conventionally calculated by means of the following expression:

$$\tau = \text{g cat hr/g cumene}$$

The contact time was modified by changing both the amount of catalyst and the flow rate.

**Analytical methods.** The preliminary runs (see later) revealed the presence in the reaction mixture of the following products: $\alpha,\alpha'$-dimethylphenylcarbinol, $\alpha$-methylstyrene, 2-phenylpropylene oxide, acetophenone, 2-phenylacrolein, benzoic acid, benzoic aldehyde, and maleic anhydride.

Some of the products, and in particular $\alpha,\alpha'$-dimethylphenylcarbinol, $\alpha$-methylstyrene, and 2-phenylpropylene oxide, were present at the different contact times only in small almost stationary amounts (about 0.1% of reaction mixture). Their presence was always revealed but their quantitative evaluation did not seem significant from a kinetic point of view. On this basis, the following analytical procedure has been developed: the reaction products, after having been weighed, were dissolved with a perfectly determined quantity of dioxane (*6*). This substance acts as a solvent and as external standard for the gas chromatographic determinations. These were performed on an ionization flame, gas chromatograph Aerograph Hg-F-600 C. Two columns were used: The first one was Bentone 34 + dodecylphthalate 1 : 1 10% on Chromosorb W, 1 m long, operated at 110°C, $P_{H_2} = 1.4$ atm, $P_{N_2} = 1.2$ atm. The second was EGS (10%) on Chromosorb

W, 2 m long, operated at 130°C, $P_{H_2} = 1.4$ atm, $P_{N_2} = 1.4$ atm.

The first column permitted determination of dioxane, cumene, and benzaldehyde, while the second one was used to determine acetophenone and 2-phenylacrolein, using as an internal standard the previously determined benzaldehyde.

Maleic anhydride and benzoic acid were determined by acidimetric and oxidimetric methods. Weighed samples of solution of the reaction products were dissolved in about 50 cc of water and the total acidity was determined with a standardized 0.05 *N* NaOH solution. On this solution five consecutive extractions of the nonacidic organic substances were preformed, each time with 10 cc of carbon tetrachloride. The remaining solution was boiled, acidified with 2 cc of sulfuric acid (1:1), and maleic anhydride was determined at 70°C with a standardized solution of $\sim$0.05 *N* $KMnO_4$.

The $CO_2$ content in the gas outcoming from the traps was measured with a thermistor gas chromatograph Carlo Erba Fractovap B/g with a silica gel column operated under standard conditions. The $CO_2$ quantity so determined reached a maximum of about 0.8%. Calculations performed on some runs showed that the amount of $CO_2$ always corresponded to the partial oxidation of cumene. We were thus enabled to leave out any total combustion process of cumene. This analytical procedure showed itself to be reliable by blank runs, and by analyzing synthetic mixtures of components.

## RESULTS

A run without catalyst was made to verify the absence of any homogeneous-phase reaction. Some preliminary runs were performed to determine the nature of oxidation products as well as the behavior of the catalyst.

The identification of reaction products was performed on a typical run made at 300°C with a contact time of 6 hr. All the reaction products, except 2-phenylacrolein were identified by gas chromatographic methods on the basis of the comparison of retention times with pure products. The most significant ones, that is benzoic acid, benzoic aldehyde, and acetophenone, were also isolated through preparative gas chromatography and confirmed as well by infrared spectroscopy. 2-Phenylacrolein (atropic aldehyde) was isolated and identified by infrared spectroscopy, quantitative analysis, and particularly by mass spectroscopy. This revealed notably the presence of two peaks corresponding to molecular weights 132 and 264. The second figure corresponds to the presence of some amount of the product obtained from 1,4-cycloaddition (*7*) of atropic aldehyde. This could slightly affect the accuracy in 2-phenylacrolein determination.

Good reproducibility of kinetic data was obtained below 360°C. By working at higher temperature it was noted that the reaction system became thermally unstable and the temperature rose to about 450°C. This phenomenon was associated with a sudden deactivation of the catalyst, revealed by an extinguishing of the reaction. The resulting black catalyst, was impossible to reactivate under our conditions. The X-ray analysis showed a low degree of crystallinity and the absence of the characteristic lines of $V_2O_5$. The infrared spectra of the powder revealed the absence of the typical bands of $V_2O_5$ in the range 750–1050 $cm^{-1}$ which corresponds to the stretching of V–O and V–O–V bands (*2*).

Kinetic runs were performed at 280°, 300°, and 320°C in a range of contact times, according to the previous definition, between 0 and 17. The results are graphically plotted in Figs. 2–4.

In order to clarify the reaction pattern, oxidation runs were conducted on some intermediates. The oxidation of acetophenone gave as main products benzaldehyde, benzoic acid, and maleic anhydride. The oxidation of $\alpha$-methylstyrene gave instead 2-phenylpropylene oxide, acetophenone, 2-phenylacrolein, benzaldehyde, and benzoic acid.

## KINETIC TREATMENT

Estimation of the influence of mass and heat transfer by means of well-known formulas (*8*) in experiments at high temperatures shows that both can be neglected.

Also the effect of internal diffusion has been evaluated at the highest temperature

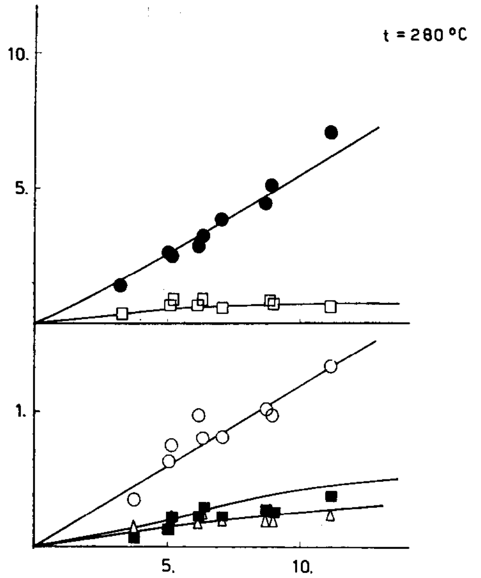


FIG. 2. Conversion percentage vs. contact time (g cat hr/g cum) at 280°C. Solid lines calculated; see text; ●, benzoic acid; □, 2-phenylacrolein; ○, maleic anhydride; ■, benzoic aldehyde; △, acetophenone.

employing the well-known procedure (*9*). The analysis showed a negligible influence of internal thermal effects; the resulting effectiveness parameter was equal to 1.34, which corresponds to an effectiveness of about 0.95. Of course at lower temperatures such an effectiveness should be taken pratically equal to unity.

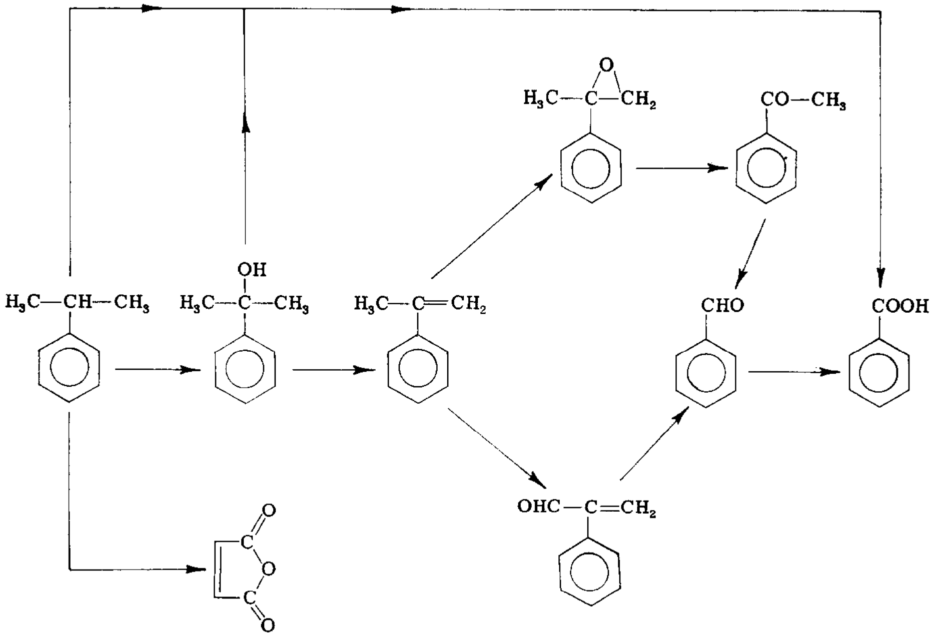
As the influence of transfer effects is of minor importance, it is possible to perform an analysis of the kinetic results on the basis of the oxidation reaction scheme.

First of all the ratio between total conversion of cumene and the conversion to maleic anhydride, that is the selectivity to maleic anhydride conversion, is practically constant at different contact times at the same temperature. The mean values of such ratios are given in Table 1. This implies that, in our range of temperature and concentration, maleic anhydride has been formed essentially from cumene through a nuclear attack parallel to that of the chain. Taking into account the results obtained from the oxidation of some intermediates (α-methylstyrene, acetophenone) it seems reasonable to propose the following oxidation scheme (I):

TABLE 1

RATIOS BETWEEN THE TOTAL CONVERSION OF CUMENE AND THE CONVERSION TO MALEIC ANHYDRIDE

| Temperature (°C): | 280° | 300° | 320° |
|---|---|---|---|
| Ratio: | 6.60 ± 0.49 | 9.75 ± 0.77 | 13.28 ± 1.44 |



Scheme (I)

The direct formation of benzoic acid from cumene can be justified by the observation that the benzoic acid concentration is already greater than that of benzaldehyde, before reaching the maximum of this compound. This statement is actually correct only for a first order reaction but it can be accepted also for nearby reaction orders. It is interesting to point out the agreement between the offered scheme of oxidation of the isopropyl group and the one proposed by Field and Meyerson (*10*) for the oxidation of cumene in the liquid phase. These authors performed the reaction in the presence of cobalt catalysts and found out that the oxidation proceeds through the following series: $\alpha$-$\alpha'$-dimethylphenylcarbinol, $\alpha$-methylstyrene, and 2-phenylpropylene oxide: small amounts of 2-phenylacrolein were also revealed. This seems to suggest an analogy in the elementary steps of homogeneous and heterogeneous catalytic oxidation.

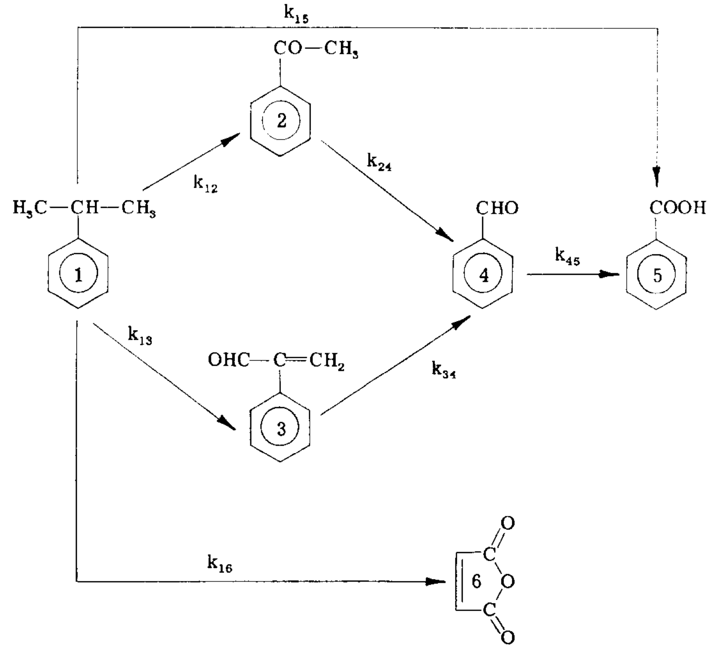
Some compounds of Scheme (I), that is, 2-phenylpropylene oxide $\alpha$-methylstyrene, and $\alpha,\alpha'$-dimethylphenylcarbinol, are present only in small and practically stationary amounts. Therefore the kinetic analysis can be performed by applying the pseudo-stationary approximation to such compounds; this means that Scheme (I) can be reduced to Scheme (II).

As a first approximation a phenomenological kinetic treatment has been made assuming pseudo-first-order rate laws for the whole process. This approach is justified by the low cumene concentration (about $0.5 \times 10^{-3}$ moles/liter), which lowers the adsorption effects on the reaction rates. According to Scheme (II) one derives the following set of kinetic equations:

$$\begin{aligned} dc_1/dt &= -(k_{12} + k_{13} + k_{16} + k_{15})c_1 \\ &= -k_1c_1 \\ dc_2/dt &= k_{12}c_1 - k_{24}c_2 \\ dc_3/dt &= k_{13}c_1 - k_{34}c_3 \\ dc_4/dt &= k_{24}c_2 + k_{34}c_3 - k_{45}c_4 \\ dc_5/dt &= k_{45}c_4 + k_{15}c_1 \\ dc_6/dt &= k_{16}c_1 \end{aligned} \tag{1}$$

where $t$ is the contact time according to the previous definition and $c_i$ is the concentration of component $i$ as indicated in Scheme (II). In fact it is possible to employ this unit thanks to the negligible variation of the total number of moles due to the high dilution of cumene in our reacting system and to the practical absence of any total combustion process.

Scheme (II) is a particular case of a set



Scheme (II)

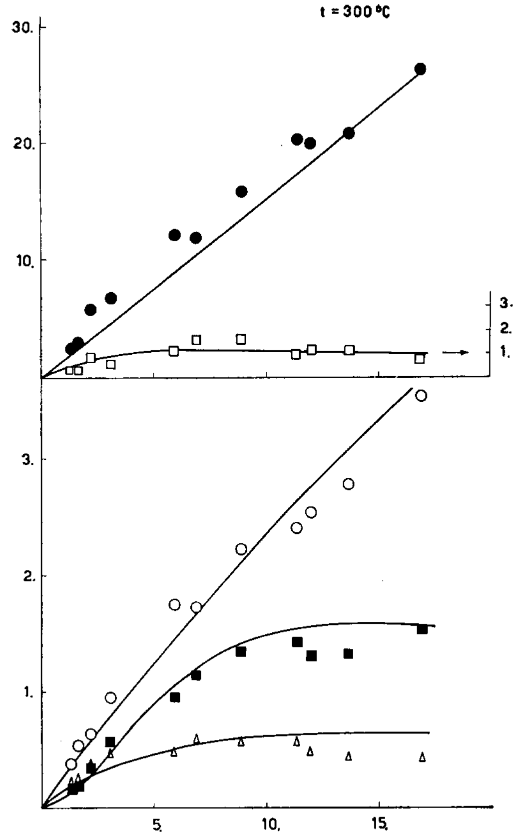


FIG. 3. Conversion percentage vs. contact time (g cat hr/g cum) at 300°C. Solid lines calculated; see text; symbols as in Fig. 2.

of successive-parallel reactions. The general expression of the rate of formation of substance $i$ in a pseudo-first-order scheme is

$$\frac{dc_i}{dt} = \sum_{j=1}^{i-1} k_{ji}c_j - k_i c_i \qquad (2)$$

where

$$k_i = \sum_{j=i+1}^{N} k_{ij} \qquad (3)$$

$N$ being the number of the components. The integration of Eq. (2) yields the following expression of the $i$th concentration:

$$c_i = \sum_{l=1}^{i} a_{il}\exp(-k_l t) \qquad (4)$$

where the coefficients $a_{il}$ can be obtained by the following recurrent formula:

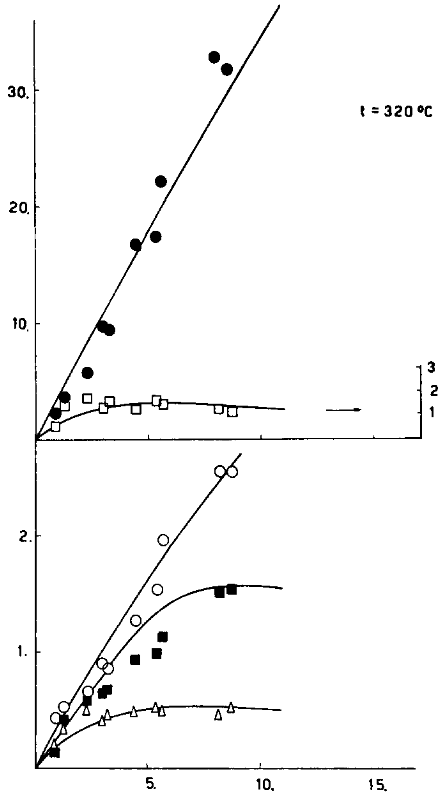


FIG. 4. Conversion percentage vs. contact time (g cat hr/g cum) at 320°C. Solid lines calculated; see text; symbols as in Fig. 2.

$$a_i = c_i^0\delta_{il} + \sum_{m=1}^{m=i-1} (\delta_{il} + \delta_{ml})(-1)^{\delta_{il}} \sum_{r=m}^{r=i-1} a_{rm}\frac{k_{ir}}{k_i - k_m} \qquad (5)$$

where $\delta$ is the Kroenecker symbol.

The calculation of the reaction rate constants $k_{ij}$ has been performed by minimizing the objective function:

$$\Phi(k_{ij}) = \sum_{i=1}^{M}\sum_{j=1}^{N}\left[\frac{(c_{ci} - c_{ei})^2}{c_{ci}c_{ei}}\right]_j \qquad (6)$$

where $M$ is the number of runs and the subscripts c and e indicate the calculated [Eq. (4)] and the experimental values, respectively. The optimization has been carried out by using the steepest descent method with automatically optimized steps. The calculations were performed on an IBM 1620-20K computer by working separately on the data at the three temperatures. The obtained values of the reaction rate constants are collected in Table 2. The full curves of Figs. 2–4 are calculated by means of these constants. The corresponding Arrhenius plots are shown in Fig. 5 and the values of the activation energies are summarized in Fig. 5.

TABLE 2
REACTION RATE CONSTANTS
(G CUMENE/HR G CAT)

| | 280°C | 300°C | 320°C |
|---|---|---|---|
| $k_1$ | $8.37 \times 10^{-3}$ | $2.36 \times 10^{-2}$ | $5.10 \times 10^{-2}$ |
| $k_2$ | 0.05 | 0.16 | 0.29 |
| $k_3$ | 0.20 | 0.35 | 0.42 |
| $k_4$ | 0.30 | 0.31 | 0.47 |
| $k_{12}$ | $3.36 \times 10^{-4}$ | $1.45 \times 10^{-3}$ | $2.28 \times 10^{-3}$ |
| $k_{15}$ | $5.06 \times 10^{-3}$ | $1.44 \times 10^{-2}$ | $3.65 \times 10^{-2}$ |
| $k_{13}$ | $1.75 \times 10^{-3}$ | $5.12 \times 10^{-3}$ | $8.50 \times 10^{-3}$ |
| $k_{16}$ | $1.22 \times 10^{-3}$ | $2.66 \times 10^{-3}$ | $3.72 \times 10^{-3}$ |

$$\text{(a)} \qquad \mathrm{I} + \mathrm{Ox} \xrightarrow{k_1} \mathrm{P} + \mathrm{Red}$$

$$\text{(b)} \qquad \mathrm{Red} + \text{oxygen} \xrightarrow{k_2} \mathrm{Ox} \qquad (7)$$

where I represents hydrocarbon; P, product Ox, an oxidation center; and Red, reduced center. Indeed by means only of the previous equations it is not possible to take into account that the adsorption of reagents on the catalyst surface hinders the progress of the reaction. This fact requires an extention of the redox mechanism; with a straightforward derivation we obtain the following rate equation:

$$r = \frac{k_1 P_\mathrm{I}}{(1 + b_\mathrm{I} P_\mathrm{I} + b_\mathrm{P} P_\mathrm{P})[(k_1 P_\mathrm{I}/k_2 P_{\mathrm{O}_2}) + 1]} \qquad (8)$$

where the $b$'s are the adsorption equilibrium constants. This equation with $b_\mathrm{I}$ and $P_\mathrm{I}$ negligible yields the known equation of Mars and Van Krevelen (*11*).

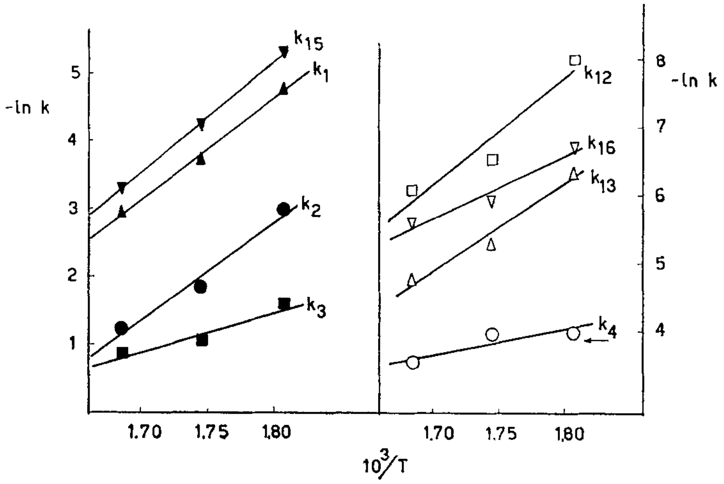


FIG. 5. Arrhenius plots of reaction rates constants. The following values of apparent activation energies (kcal/mole) were obtained: $E_1 = 29.36$; $E_2 = 28.62$; $E_3 = 12.10$; $E_4 = 7.21$; $E_{12} = 31.26$; $E_{15} = 32.07$; $E_{13} = 25.73$; $E_{16} = 18.01$. Subscripts have the same meaning as in Table 2.

## DISCUSSION

Except for some small discrepancies concerning the conversion to benzoic acid at 300°C, the kinetic analysis performed shows a satisfactory agreement with the experimental results.

The rate equation of hydrocarbon oxidation can be derived from a redox mechanism of the following type:

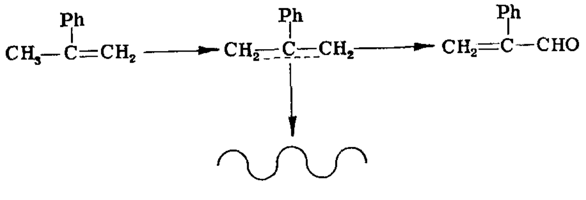
It was shown that the reoxidation reaction (b) of active centers is fast in this range of temperatures (*12*). In a recent investigation (*13*) on the methyl alcohol oxidation on pure $V_2O_5$ the value of the constant of catalyst oxidation $k_2$, has been evaluated at 280°C. Such a result enables us to calculate the value of the ratio $(k_1 P_\mathrm{I}/k_2 P_{\mathrm{O}_2})$, for the cumene oxidation at 280°C. Taking into account the different surface area it was possible to obtain a rough value of about 0.005. Therefore Eq. (8) can be simplified as follows:

$$r = k_1P_\mathrm{I}/(1 + b_\mathrm{I}P_\mathrm{I} + b_\mathrm{P}P_\mathrm{P}) \qquad (9)$$

This equation seems to indicate that at low temperature, significative deviation from the first order rate law can be due only to the effect of the adsorption of reagents. The low concentration of cumene (partial pressure about 9 mm) at which our kinetic runs were performed decreases such effects and justifies the employment of the pseudo-first-order scheme [Eq. (1)]. Another interesting remark derives from the observed behavior of the catalyst at 350°–360°C, at which temperatures a fast over-reduction of the catalyst took place. The fact reveals in a dramatic way the intervention of the reticular oxygen in step (b) of Eqs. (7). This range of temperatures corresponds to the bulk Tamman temperature, as pointed out by Clark and Berets (*14*), through thermoelectric measurements.

On the whole it was shown that under mild temperature conditions the oxidation occurs through a nuclear attack that yields maleic anhydride as well as through an attack on the alkyl group that finally yields benzoic acid. This scheme is in agreement with the one proposed by Simard (*4*) for the oxidation of *o*-xylene. The formation of 2-phenylacrolein through the oxidation of $\alpha$-methylstyrene formally recalls the propylene oxidation on copper oxide to acrolein.

This process is normally interpreted through the formation of a surface allyl radical as follows (*15*):



$$\mathrm{CH_3}-\overset{\mathrm{Ph}}{\mathrm{C}}=\mathrm{CH_2} \longrightarrow \mathrm{CH_2}\cdots\overset{\mathrm{Ph}}{\mathrm{C}}\cdots\mathrm{CH_2} \longrightarrow \mathrm{CH_2}=\overset{\mathrm{Ph}}{\mathrm{C}}-\mathrm{CHO} \qquad (10)$$

## Acknowledgment

We are indebted to Italian Consiglio Nazionale delle Ricerche for financial aid.

## References

1. Morita, S., *Nippon Kagaku Zasshii* **79,** 1230–1236 (1958).
2. Frederiksson, L. D., and Hausen, D. M., *Anal. Chem.* **35,** 818 (1963).
3. Tarama, K., Teranishi, S., Yoshida, S., and Tamura, N., *Proc. Intern. Congr. Catalysis 3rd, Amsterdam, 1964* (North-Holland Publ. Co., Amsterdam, 1965).
4. Simard, G. L., Steger, J. F., Arnott, R. J., and Siegel, L. A., *Ind. Eng. Chem.* **47,** 1424 (1955).
5. "Selected Values of Properties of Hydrocarbons and Related Compounds," Table 5 k, p. 2. American Petroleum Institute.
6. Bernardini, F., Ramacci, M., and Paolacci, A., *Chim. e Ind.* **47,** 485 (1965).
7. Patai, S., "The Chemistry of Alkenes." Interscience, New York, 1964.
8. Yoshida, F., Ramaswami, D., and Hougen, O. A., *A. I. Ch. E. J.* **8,** 5 (1962).
9. Satterfield, C. M., and Sherwood, T. H., "The Role of Diffusion in Catalysis." Addison Wesley, Reading, Massachusetts, 1963.
10. Fields, E. K., and Meyerson, S., International Oxidation Symposium, Stanford Research Institute, San Francisco, 1967.
11. Mars, P., and Van Krevelen, D. W., *Chem. Eng. Sci.* **3,** Spec. Suppl. 41 (1954).
12. Roiter, V. A., *Kinetika i Kataliz* **1,** 63 (1960).
13. Bhattacharryya, S. K., Janakiram, K., and Ganguly, N. D., *J. Catalysis* **8,** 128 (1967).
14. Clark, H., and Berets, D. J., *Advan. Catalysis* **9,** (1957).
15. Tipper, C. H. F., "Oxidation and Combustion Reviews." Elsevier, New York and Amsterdam, 1965.