

Hydrogen Transfer Reactions

IV. Substituent Effect in the Reduction of Benzaldehydes by Isopropyl Alcohol Catalyzed by Alumina¹

N. VENKATASUBRAMANIAN, D. V. RAMANA, AND C. N. PILLAI²

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Received June 14, 1976

A linear Hammett correlation is reported for the reduction of substituted benzaldehydes by isopropyl alcohol catalyzed by alumina containing 2.2% (by weight) sodium ions, at 300°C in the vapor phase. The positive nature of the slope supports the hydrid transfer mechanism proposed for this reduction.

INTRODUCTION

Alumina and other catalysts are known to catalyze hydrogen transfer reactions both in the vapor phase (1-4) and in the liquid phase (5, 6). Stereochemical studies on the reduction of (-)-menthone with isopropyl alcohol (7) catalyzed by alumina in the vapor phase have led to the conclusion that the reaction involves a direct transfer of hydrogen from an adsorbed alcohol molecule to an adsorbed ketone molecule. This paper describes the study of substituent effects in the reduction of benzaldehydes by isopropyl alcohol over alumina. The result supports a hydrid transfer mechanism.

EXPERIMENTAL

Pure alumina and alumina impregnated with 2.2% Na⁺ (2.2% Na⁺/Al₂O₃) were

¹ Taken in part from the Ph.D. dissertation of D.V.R., Indian Institute of Technology, Madras (1970). For Part III of the series, see: Unni, M. P. K., Santhanagopalan, S., and Pillai, C. N., *J. Indian Chem. Soc.*, 582 (1973).

² To whom reprint requests should be addressed.

used in the present study. The catalysts were prepared as reported earlier (1). The reactants were introduced into the reactor (7) at the required flow rate using a syringe pump. The products for the first 15 min were rejected and the products for the next 30 min were collected and analyzed by gas chromatography. Material balance and stoichiometry were checked for each reaction. The catalyst activity was verified after each reaction. In the present study the activity remained constant throughout.

RESULTS AND DISCUSSION

The reaction between carbonyl compounds (cyclohexanone and substituted benzaldehydes in the present case) and isopropyl alcohol over 2.2% Na⁺/Al₂O₃ at 300°C gave acetone and the alcohols derived from the carbonyl compounds as the only products. Dehydration of alcohols did not take place on this catalyst. However, on pure alumina dehydration of the alcohols was a competing reaction.

Figure 1 shows the results of reaction between mixtures of isopropyl alcohol and

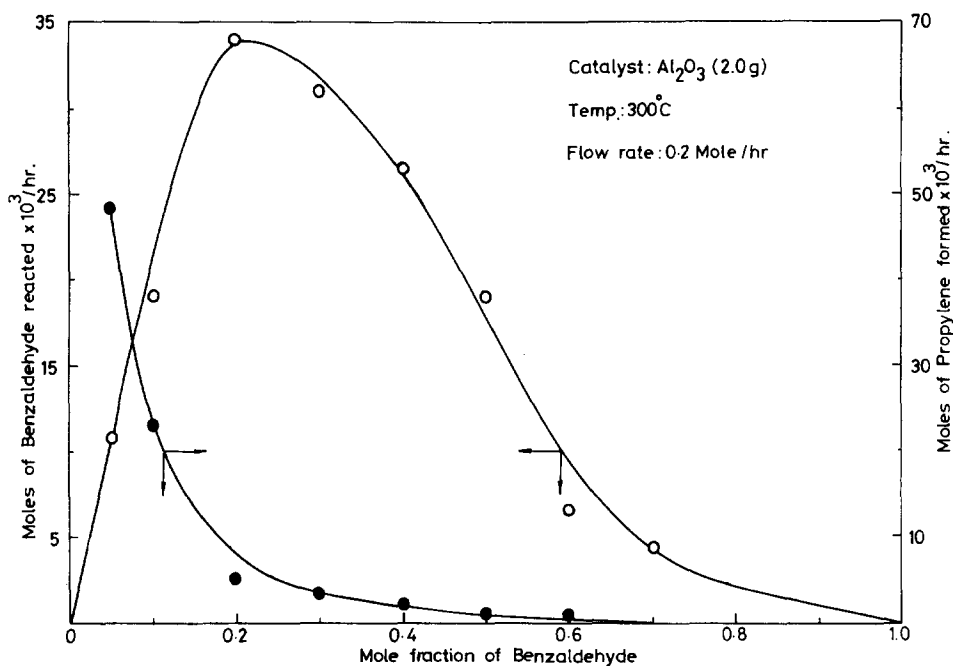


FIG. 1. Reaction of benzaldehyde-isopropyl alcohol mixtures of different compositions.

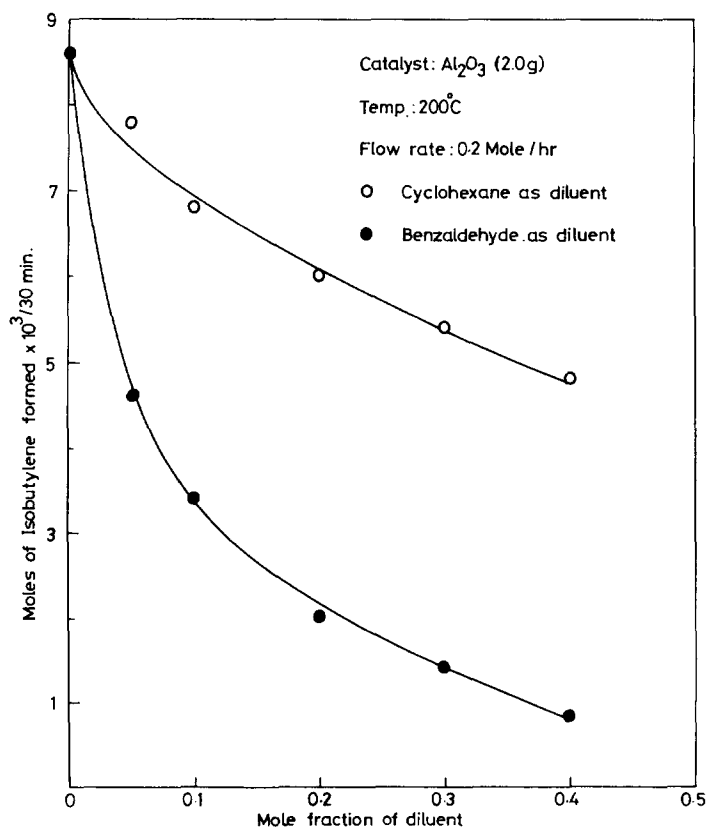


FIG. 2. Dehydration of *t*-butyl alcohol-diluent studies.

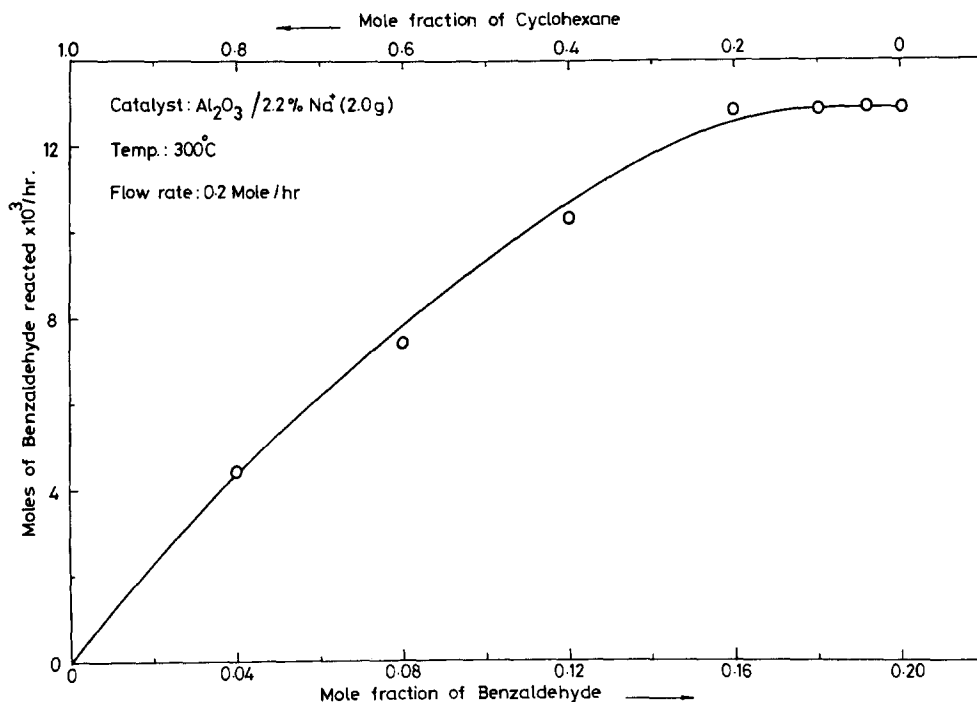


FIG. 3. Reaction of a 1:4 molar mixture of benzaldehyde and isopropyl alcohol with cyclohexane as diluent.

benzaldehyde of different compositions over pure alumina at 300°C . Propene, by the dehydration of isopropyl alcohol, and benzyl alcohol and acetone, by the hydrogen transfer reaction, were the products. The latter two products were formed in equimolar quantities. From Fig. 1 it can be seen that benzaldehyde strongly inhibits the dehydration of isopropyl alcohol. This inhibiting effect is partly due to the parallel reaction undergone by isopropyl alcohol, namely, hydrogen transfer. To determine whether this inhibition is also due to competitive adsorption by benzaldehyde on the dehydration sites, some studies with *t*-butyl alcohol were carried out. Figure 2 shows the effect of benzaldehyde and also of cyclohexane on the dehydration of *t*-butyl alcohol. This alcohol can undergo only dehydration and not hydrogen transfer. Benzaldehyde does not undergo any reaction and its role is only that of a diluent. From the figure it can be seen that benzaldehyde strongly inhibits the dehydration reaction,

unlike cyclohexane, which can be considered to be an inert diluent and whose inhibition effect is only due to dilution. At low partial pressures of the diluent, where cyclohexane has very little effect, benzaldehyde has a strong poisoning effect. This clearly shows that benzaldehyde and *t*-butyl alcohol, and by analogy isopropyl alcohol, compete for the same adsorption sites.

It was necessary to determine whether the hydrogen transfer reaction occurred by the interaction of the adsorbed alcohol molecules with the adsorbed aldehyde. This was done by studying the effect of an inert diluent (cyclohexane) on the rate of reaction of a 1:4 molar mixture of benzaldehyde and isopropyl alcohol on 2.2% $\text{Na}^+/\text{Al}_2\text{O}_3$. This composition of mixture was chosen because it corresponded to the maximum reaction rate, as discussed later. The results are given in Fig. 3. It can be seen that at low cyclohexane content, the rate of hydrogen transfer reaches a maximum and remains independent of cyclohexane concen-

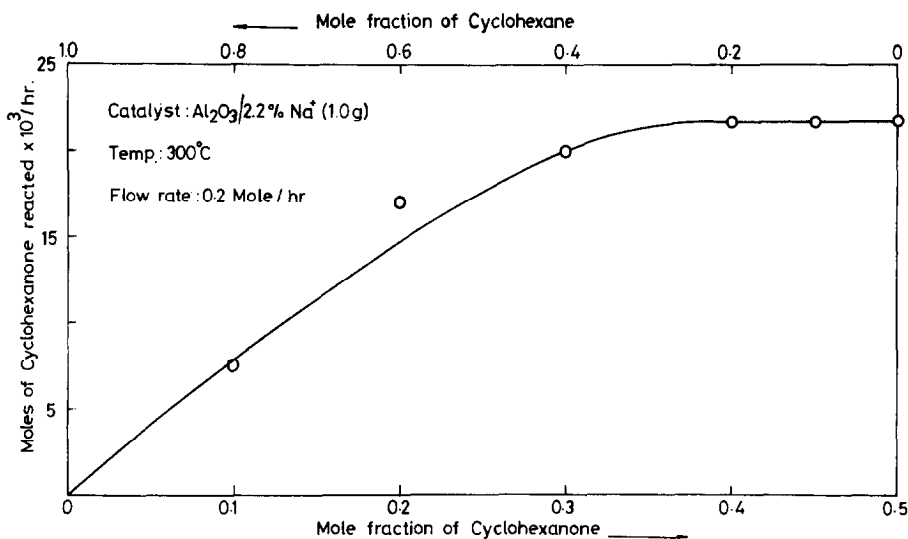


FIG. 4. Reaction of a 1:1 molar mixture of cyclohexanone and isopropyl alcohol with cyclohexane as diluent.

tration. This region must correspond to partial pressures of benzaldehyde and isopropyl alcohol at which they together

saturate all the adsorption sites. The horizontal portion of the curve could not have been obtained if either one of the reactants

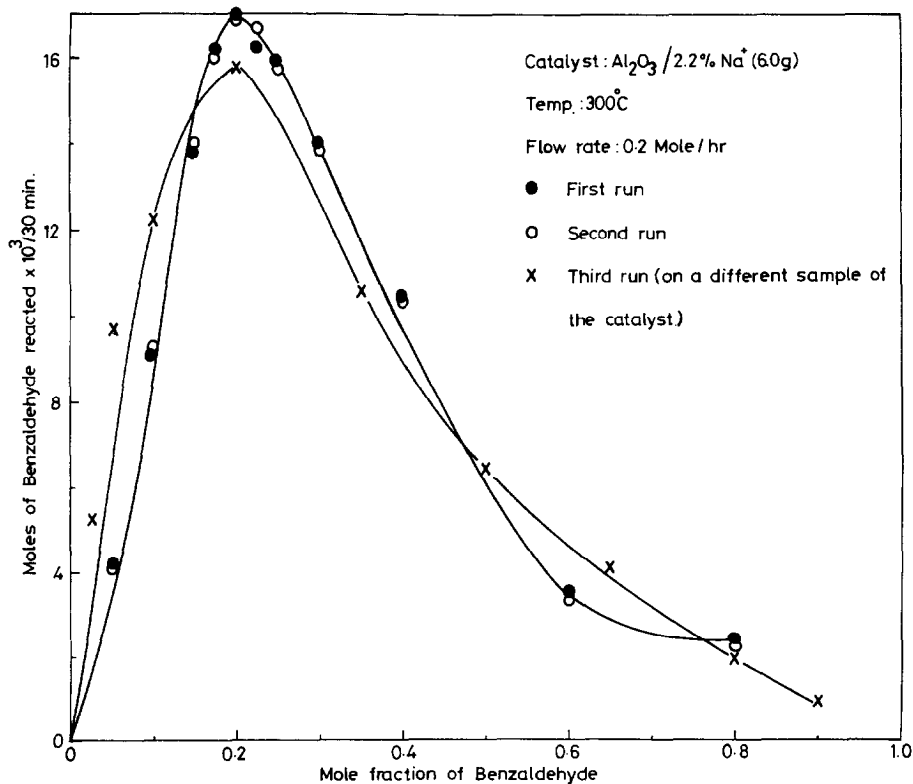


FIG. 5. Reduction of benzaldehyde with isopropyl alcohol at different mole fractions.

TABLE 1
Hammett's Plot at Maximum Molar Conversions

Reactant No.	Max. moles reacted	log ($M \times 10^2$)	At mole fraction	Hammett σ value	Substituent
1. Benzaldehyde	0.0170	0.2304	0.2	0	H
2. <i>p</i> -Methylbenzaldehyde	0.0124	0.0934	0.175	-0.170	<i>p</i> -CH ₃
3. <i>p</i> -Chlorobenzaldehyde	0.0256	0.4082	0.2	+0.226	<i>p</i> -Cl
4. <i>p</i> -Methoxybenzaldehyde	0.0108	0.0334	0.19	-0.226	<i>p</i> -CCH ₃

was reacting from the gas phase. A similar curve was obtained for the hydrogen transfer reaction between cyclohexanone and isopropyl alcohol when the effect of dilution by cyclohexane on a 1:1 molar mixture of the two was studied (Fig. 4).

From the foregoing it can be concluded that the hydrogen transfer reaction takes place by a Langmuir-Hinshelwood mechanism and that both the reactants are ad-

sorbed on the same kind of adsorption sites.

In order to evaluate the substituent effects, the rates of reaction of benzaldehyde and three substituted benzaldehydes with isopropyl alcohol on 2.2% Na⁺/Al₂O₃ were studied. The results were fitted into a Hammett plot using initial rates instead of rate constants, a procedure justified if the initial concentrations of the reactants

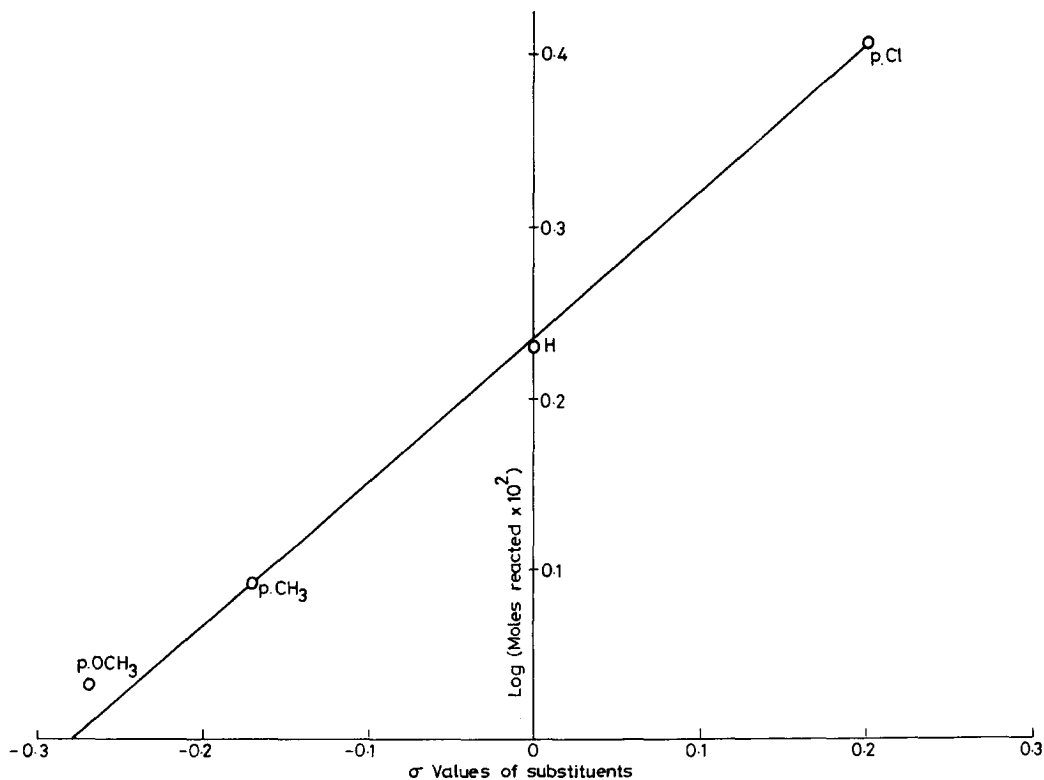


FIG. 6. Hammett's plot of the reduction of substituted benzaldehydes with isopropyl alcohol at maximum rates.

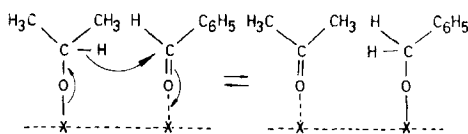


FIG. 7. Proposed mechanism for hydride transfer.

on the surface are the same. Partial pressures at which this condition was satisfied were established in the following manner, described in detail for the benzaldehyde-isopropyl alcohol system.

Mixtures of benzaldehyde and isopropyl alcohol were prepared in which the mole fraction of benzaldehyde varied from 0.05 to 0.8. The total number of moles of benzaldehyde and isopropyl alcohol was kept the same in all the mixtures. The mixtures were passed over 2.2% $\text{Na}^+/\text{Al}_2\text{O}_3$ catalyst at identical contact times (0.2 mole/hr), and the relative rates as represented by the number of moles of benzaldehyde reacted in a specific time were determined. When these rates were plotted against mole fractions, a maximum was obtained at a mole fraction of benzaldehyde

of about 0.2 (Fig. 5). Similar maxima were also obtained for the substituted benzaldehydes (Table 1).

Assuming a Langmuir-Hinshelwood mechanism for the hydrogen transfer reaction, with the reactants competing for the same sites, the maximum rate will correspond to the situation where the product of the surface concentrations of the two reactants is maximum. Under these conditions,

$$\text{rate}_{(\max)} = K[a][b]_{(\max)},$$

where $[a]$ and $[b]$ are the surface concentrations of the two reactants and $[a]$ must be equal to $[b]$ since $[a] + [b]$ is equal to the total number of adsorption sites and is a constant. Hence maximum rate would correspond to the situation where the surface is equally covered by the two reactants. Logarithms of the maximum rates in each case were plotted against Hammett σ values (Table 1, Fig. 6). A straight line with a positive slope ($\rho = +0.76$) was obtained, as expected for a mechanism involving a hydride transfer to the electron-

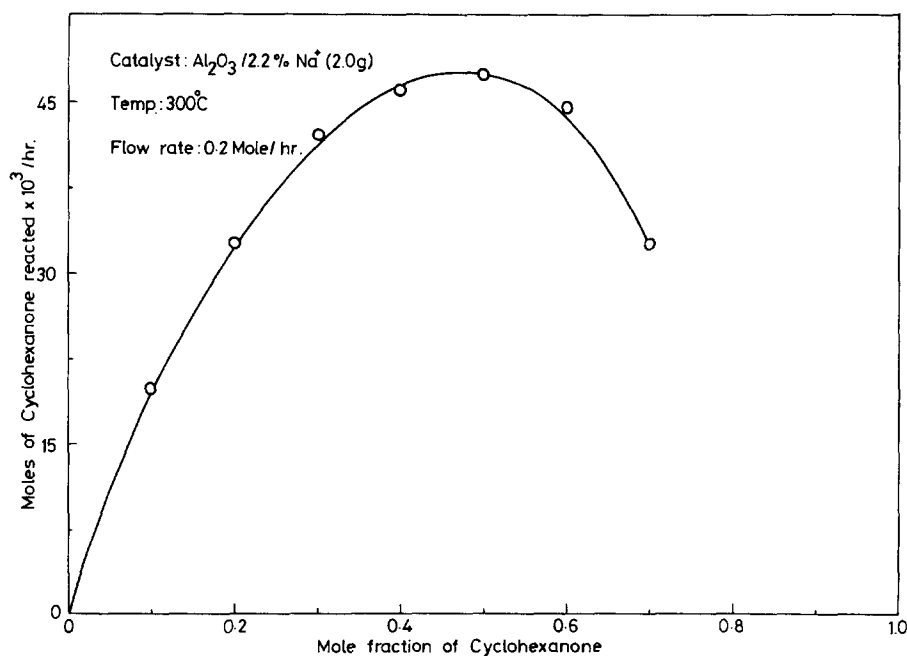


FIG. 8. Reduction of cyclohexanone with isopropyl alcohol at different mole fractions.

deficient carbonyl carbon. The proposed mechanism (Fig. 7) (?) was thus supported.

For all the four benzaldehydes the rate maxima were very nearly at the same partial pressure, indicating nearly the same adsorption coefficients for the different benzaldehydes. This would predict that even at some mole fraction other than the ones corresponding to the maxima, a linear relationship should be obtained. Rates at an arbitrarily chosen mole fraction of benzaldehydes of 0.4 were plotted. The linear correlation was not as good as in the earlier plot.

A rate versus mole fraction plot for cyclohexanone-isopropyl alcohol mixtures is given in Fig. 8. The maximum in this case occurs at a mole fraction of cyclohexanone of about 0.5, indicating that cyclohexanone is less strongly adsorbed than the series of benzaldehydes studied.

ACKNOWLEDGMENTS

The authors are indebted to the Council of Scientific and Industrial Research, New Delhi, the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support, and Professor J. C. Kuriacose for valuable discussions.

REFERENCES

1. Ramana, D. V., and Pillai, C. N., *Canad. J. Chem.* **47**, 3705 (1969).
2. Niiyama, H., and Echigoya, E., *Bull. Chem. Soc. Japan* **45**, 938 (1972).
3. Okamoto, Y., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Japan* **45**, 3207 (1972).
4. Kibby, C. L., and Hall, W. K., *J. Catal.* **31**, 65 (1973).
5. Hruby, V. J., *Proc. N. Dak. Acad. Sci.* **16**, 12 (1962); *Chem. Abstr.* **62**, 1589 (1965).
6. Posner, G. H., and Ranquist, A. W., *Tetrahedron Lett.* **42**, 3601 (1975).
7. Ramana, D. V., and Pillai, C. N., *Ind. J. Chem.* **8**, 1186 (1970).