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Syntheses of Citral and Citronellal by the Dehydrogenation of Geraniol Using Cu, Cu-Zn, Cu-Cr, and ZnO Catalysts

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The present paper describes the study of the syntheses of citral and citronellal by the catalytic dehydrogenation of geraniol with Cu, Cu-Zn, Cu-Cr, and ZnO catalysts under an atmospheric or a reduced pressure in vapor and liquid-phase systems. The following results were obtained: (1) the vapor-phase dehydrogenation with the Cu-Zn catalyst, conducted at a reduced pressure, was found to be most favorable, (2) when using this catalyst at 230°C, the addition of citronellal as a hydrogen acceptor prior to the dehydrogenation increased the yield of the citral from 50% to 85% (at 185°C, the highest yield of citronellal, 70%, was obtained). The composition of the product was analyzed by means of G. L. C. The reaction scheme under various conditions is also described briefly.

Citral is a raw material for the increasingly-important ionone and Vitamine A, whereas citronellal is a raw material for menthol and hydroxycitronellal. Geraniol, a basic material for both citral and citronellal, has recently become available by means of an entirely synthetic process, instead of having to be derived from the limited natural-product source. Therefore, the present authors, in the course of their study of the synthesizing of important monoterpene compounds used for perfumery, have attempted to make citral and citronellal by the catalytic dehydrogenation of geraniol.

Concerning the present studies, only a few papers and patents have been published. Bouveault

reported the quantitative conversion of geraniol into citral in the catalytic dehydrogenation of geraniol over copper at 200°C;¹⁾ Treibs observed the formation of citronellal in the distillation of geraniol at an atmospheric pressure in the presence of copper²⁾; a Russian patent described the vapor-phase dehydrogenation of geraniol at 220—230°C at a pressure of 100 mmHg, using the Cu-Cr catalyst (9% citral and 65% citronellal were thus produced)³⁾; a Japanese patent⁴⁾ claimed the use of methyl ethyl ketone or butyraldehyde as a hydrogen acceptor in the liquid-phase catalyzed dehydrogenation, using a Raney-Cu, Cu-Zn or Cu-Cr catalysts, thus showing the possibility of

1) L. Bouveault, *Bull. Soc. Chim. France* (4) 3, 119 (1908).

2) W. Treibs and H. Schmidt, *Ber.*, **60**, 2335 (1927).

3) B. H. Kapabas, U.S.S.Pat. 118498 (1958).

4) T. Hashimoto and T. Shibuya, Japanese Pat. 15007 (1965).

producing citral in an improved yield of 42–43%.

The present paper will describe the syntheses of citral and citronellal by the catalyzed dehydrogenation of geraniol with a Cu, Cu-Zn, Cu-Cr, or ZnO catalyst under varying experimental conditions.

Experimental

Materials. The geraniol was purchased from the ABRAC Company, Ltd.; bp 99°C/5 mmHg, n_D^{20} 1.4740, d_4^{20} 0.8863. Its purity was confirmed by G.L.C. to be 98.0%. The citronellal was obtained from citronellal oil (from Formosa) by a previously described⁵⁾ method; bp 72–73°C/6 mmHg, d_4^{20} 0.8594, n_D^{20} 1.4492, $[\alpha]_D^{25} +10.8^\circ\text{C}$.

Catalysts Used. Cu-Cr-, Cu-Zn-, and ZnO-type catalysts were supplied by the Nikki Chem. Company, Ltd. Various forms of the catalyst suitable for each dehydrogenation system were used; (a), (b) and (c) were tableted catalysts 6 mm in dia. and 6 mm high, 6 mm in dia. and 3 mm high, and 3 mm in dia. and 3 mm high respectively, while (d) was a powder. The copper catalyst was used in the form of a copperwire gauze (50 mesh), as has been described by Bouveault.¹⁾

Apparatus Used for Dehydrogenation. The general structure of the apparatus used for the dehydrogenation of geraniol is presented in Fig. 1. Geraniol vapor was supplied through an evaporator (2) into a reactor (3), and the reaction product was collected in a receiver (6). The catalysts were packed in the constant-temperature region of the reaction tube, as shown in Fig. 1. The evaporator (2) was heated to approximately 205°C, using Bay oil as the heating medium.

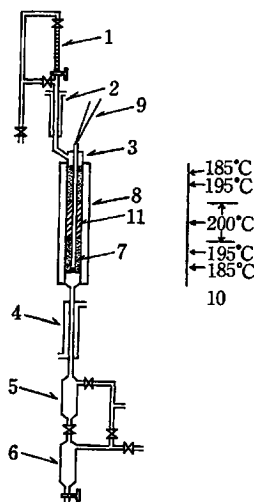


Fig. 1. Catalytic dehydrogenation apparatus.

1 Feed burette, 2 Evaporator, 3 Reactor (dia. 28 mm, length 400 mm), 4 Condenser, 5 Product receiver, 6 Product receiver, 7 Glass Rasing ring, 8 Electric-furnace, 9 Thermocouple, 10 Temperature gradient in reactor, 11 Catalyst

A portion of the glass tube leading from the evaporator to the reaction tube was also heated to 205°C by using a ribbon heater, thus keeping the temperature gradient along the reaction tube constant.

Vapor-phase Dehydrogenation Procedure at Atmospheric Pressure. After the packed catalyst had been activated with hydrogen, the reaction tube was allowed to cool to room temperature in a hydrogen stream; then the hydrogen was turned off, and nitrogen was introduced for 30 min at a rate of 500 ml/min. Then geraniol vapor was passed through the reacting zone of the reaction tube (kept at 200°C) under various conditions. After the reaction, the product collected in the receiver was taken with 100 ml of ether. The ether solution was neutralized with an aqueous solution of sodium carbonate, washed with water, dehydrated with sodium sulfate, and submitted to the evaporation of ether on a water bath to give an oily product (97–98% by weight for geraniol supplied). The composition of the product was determined by G.L.C. In the case of using a hydrogen acceptor, ethylene⁶⁾ (obtained commercially; purity 99.2%), rather than nitrogen, was passed through at a rate of 300 ml/min after the activation of the catalyst with hydrogen; acetone⁷⁾ or quinoline⁸⁾, mixed in geraniol, was passed through the reacting zone under a nitrogen flow.

Vapor-phase Dehydrogenation Procedure at Reduced Pressure. After the treatment of the catalyst with hydrogen and subsequent displacement with nitrogen much as has been described above, the gas inlet-cock was closed. Then the reaction system was evacuated to a certain reduced pressure, and the geraniol vapor was supplied to the reaction tube at a given L.S.V. The product was treated much as in the dehydrogenation at an atmospheric pressure. When the copper catalyst was used, the dehydrogenation was carried out under the same conditions as have been described by Bouveault.¹⁾

Liquid-phase Dehydrogenation Procedure at Atmospheric Pressure. A given amount of a catalyst was placed in a 300-ml four-necked flask equipped with an air-tight stirrer, a hydrogen inlet-tube, a Stark-Dean trap (fitted with a hydrogen outlet-tube to remove any water formed during the activation of the catalyst with hydrogen), and a thermocouple in contact with the catalyst placed at the bottom of the flask. The catalyst was heated at 200°C in an oil bath, and hydrogen was passed through the catalyst at a rate of 200 ml/min for 30 min; then the flask was displaced with nitrogen for 30 min at the rate of 200 ml/min. Thereupon, geraniol (50 g, 0.32 m) was put in the flask, and it was kept at 200°C with stirring under a nitrogen flow. The progress of the reaction was followed by G.L.C., by which the end point of the reaction was determined.

Identification and Analysis of the Product by G.L.C. In the selective dehydrogenation of geraniol to form citral or citronellal, the isolation of each product was attempted by means of a precise fractional distillation technique. The gas chromatograph Kotaki

6) W. Reeve and H. Adkins, *J. Am. Chem. Soc.*, **62**, 2874 (1940).

7) L. C. Andess, *ibid.*, **64**, 1456 (1942).

8) K. W. Rosenmund and F. Z. Zetsche, *Ber.*, **54**, 1002 (1921).

5) P. Z. Bedoukian, "Perfumery and Flavoring Synthetics," Elsevier Publishing Company, Amsterdam (1967), p. 107.

GU-21, with a thermal conductivity detector, was used, and the quantitative analysis of the composition of the product was based on the normalization method. The experimental conditions were as follows; a stainless column (dia., 3 mm; length, 2 m) packed with Dia Base A, 60–80 mesh, which was coated with 10% of Silicone DC 550, 15% of PEG 1500 and 5% of PEG 4000; helium inlet pressure, 0.78 kg/cm², flow rate of 30 ml/min; column temperature, 180°C; split temperature, 250°C; sensitivity, 8 mv; chart speed, 0.5 cm/min. The standard materials used in this analysis were prepared according to the methods described in the literature or were obtained by rectifying commercially-available chemicals. Each of these materials was found to give a single peak in its respective gas chromatogram; myrcene (from the ABRAC Company, Ltd.) bp 39°C/4 mmHg, n_D^{20} 1.4690, d_{40}^{20} 0.7883; limonene (from orange oil purchased from the Polak Frutal Company, Ltd.), bp 40°C/4 mmHg, n_D^{20} 1.4717, d_{40}^{20} 0.8407; ocimene was prepared from linalool according to the Naves method,⁹⁾ bp 42°C/4 mmHg, n_D^{20} 1.4861, d_{40}^{20} 0.8655; citronellol (from the ABRAC Company, Ltd.), bp 100°C/6 mmHg, n_D^{20} 1.4539; d_{40}^{20} 0.8572; citronellal was the same as that described in the preceding section; citral was prepared by the known method⁹⁾ from lemon-grass oil; bp 102–104°C/6 mmHg, n_D^{20} 1.4881, d_{40}^{20} 0.8962; geraniol (from the ABRAC Company, Ltd.), bp 100–102°C/6 mmHg, n_D^{20} 1.4492, d_{40}^{20} 0.8594; isopulegol (from the Tokyo Kasei Ind. Compnay, Ltd.), a mixture of 20% neo-isopulegol, 75% isopulegol and 5% iso-isopulegol (by

G. L. C.), bp 74–78°C/6 mmHg, n_D^{20} 1.4679; d_{40}^{20} 0.9074.

Activity of the Catalyst Used. As may be seen in Table 1, the Cu-Zn catalyst gave a similar product distribution when 15 ml of geraniol was supplied for the 2nd and 3rd runs under the experimental conditions indicated. The results of the first run were considered to be inadequate and unreliable. On the basis of the above results and on the technical information supplied by the Nikki Chem. Company, Ltd., the data collected on the second run of 15 ml of geraniol was considered pertinent to this experiment (see Table 1).

Results and Discussion

Product Distribution in the Catalyzed Vapor-phase Dehydrogenation of Geraniol at Atmospheric Pressure. The results obtained are summarized in Tables 2 and 3.

a) Comparison of the Catalysts. In the dehydrogenation of geraniol over copper at 200°C or 250°C (see Table 2), contrary to Bouveault's finding indicating the quantitative transformation of geraniol into citral, a very small conversion of geraniol and, in addition, the formation of various by-products, such as terpene hydrocarbons as well as citral and citronellal, was observed; citral had a yield of only 20%. With the ZnO catalyst system, at a reaction temperature between 190°C and 230°C,

TABLE 1. CHANGES IN PRODUCT DISTRIBUTION *vs.* SUPPLYING TIME OF GERANIOL (15 ml) USING Cu-Zn CATALYST
Composition of products by G. L. C. (wt%)

Time of supplying	Terpene hydrocarbons	Citronellal	Isopulegol	Citronellol	Citral	Geraniol
1	17.0	30.9	12.9	6.5	32.7	
2	14.7	38.0	15.5	4.9	26.9	
3	14.4	39.2	14.4	6.1	25.8	

* The experimental condition was identical to that indicated in the first run of Table 3.

TABLE 2. VAPOR-PHASE DEHYDROGENATION OF GERANIOL USING THE REDUCED COPPER AT A REDUCED PRESSURE

Run	Reaction temperature	Reduced pressure mmHg	Geraniol flow rate	Composition of products by G.L.C. (wt%)			
				Terpene hydro-carbon	Citronellal	Citral	Geraniol
1	200°C	4–5	65 ml/hr	7.3	7.2	20.6	64.9
2	200°C	41–45	65 ml/hr	11.7	10.1	17.1	61.1
3	230°C	3–4	65 ml/hr	4.7	5.9	16.3	73.1
4	230°C	4	21 ml/hr	4.9	7.1	21.2	66.8
5	250°C	4	65 ml/hr	4.5	7.5	18.7	69.3
6	250°C	102	65 ml/hr	21.0	16.8	21.1	41.1
7*	200°C	4–5	65 ml/hr	5.4	5.3	22.9	66.4
8*	200°C	40–45	65 ml/hr	8.9	8.6	20.1	62.4

* Run 7, 8: Dehydrogenation was carried out using the apparatus described in Fig. 1.

9) Y. R. Naves and F. Bondavalli, *Helv. Chim. Acta*, **48**, 563 (1965).

TABLE 3. VAPOR-PHASE CATALYTIC DEHYDROGENATION OF GERANIOL AT ATMOSPHERIC PRESSURE

Run	Starting material, hydrogen acceptor, weight ratio for geraniol	Atmosphere, flow rate	Catalyst*, ml	Reaction temperature °C	L.S.V. l/hr	Terpene hydrocarbons	Composition of products by G.L.C. (wt%)			
							Citronellal	Isopulegol	Citronellol	Citral
1	Geraniol	N ₂ , 500 ml/min	Cu-Zn, 25	200	0.25	14.7	38.0	15.5	4.9	26.9
2	Geraniol	N ₂ , 500 ml/min	Cu-Cr, 25	200	0.25	20.0	37.8	12.2	6.8	23.2
3	Geraniol	N ₂ , 500 ml/min	ZnO, 30	230	0.30	25.0	0	0	0	75.0
4	Geraniol-acetone*** (1:1)**	N ₂ , 500 ml/min	Cu-Zn, 25	200	0.40	17.6	25.8	15.2	6.7	24.7
5	Geraniol	Ethylene*** 300 ml/min	Cu-Zn, 25	200	0.50	9.7	45.2	16.0	3.4	25.7
6	Geraniol, quinoline*** (1:0.5)**	N ₂ , 500 ml/min	Cu-Zn, 25	200	0.30	9.8	13.8	3.7	5.5	26.9
7	Citral	N ₂ , 500 ml/min	Cu-Zn, 25	200	0.30	14.8	10.1	6.1	0	69.0
8	Citral	N ₂ :H ₂ =10:1, 200 ml/min	Cu-Zn, 25	200	0.30	11.4	19.8	10.1	0	58.7

* Form of the catalyst used was of (a). ** by weight *** Hydrogen acceptor.

TABLE 4. LIQUID-PHASE CATALYTIC DEHYDROGENATION OF GERANIOL

Run	Catalyst*, wt% for geraniol	Geraniol g	Hydrogen acceptor added, g (molar ratio to geraniol)	Reaction temperature °C	Reaction time hr	Terpene hydrocarbons	Composition (%) of products by G.L.C. (wt%)			
							Citronellal	Isopulegol	Citronellol	Citral
1	Cu-Zn, 2.0	50		200-204	3.0	0	21.5	20.6	32.5	23.2
2	Cu-Zn, 2.0	50		200-204	4.0	0	12.8	29.3	32.6	23.3
3	Cu-Cr, 2.0	50		201-205	3.5	13.2	5.3	18.3	32.0	25.5
4	Cu-Zn, 2.0	50	Citronellal (1:0.5)	200-205	2.5	3.9	11.1	22.2	16.8	23.3 (53%)**
5	Cu-Zn, 2.0	50	Citronellal (1:1.3)	200-205	3.5	6.1	8.8	39.5	21.0	16.8 (47%)**
6	Cu-Zn, 5.0	50	Cyclohexanone (1:1)	180-185	3.5	0	17.2	6.0	21.2	41.0 (48.0%)**

* Form of the catalyst used was of (d). ** Yield for geraniol reacted.

no dehydrogenation reaction occurred; the terpene hydrocarbon was given in a yield of 25%, while 75% of unreacted geraniol was recovered, indicative of the inefficient catalysis of the ZnO catalyst in the dehydrogenation.

The Cu-Zn and Cu-Cr catalyst systems gave similar product distributions: citral (26%; 23% (theor.)), citronellal (37%; 38%), isopulegol (15%; 12%), terpene hydrocarbons (14%; 20%), including myrcene, limonene and ocimene, and citronellol (4%; 6%). Although the difference in the product distribution was not remarkable between them, the Cu-Zn catalyst was found to be preferable to the Cu-Cr catalyst because of its smaller formation of terpene hydrocarbons and its increased yield of citral (see Table 3).

From the above results, it was concluded that the copper or ZnO system showed less catalytic activity in the dehydrogenation of geraniol, and that, with regard to the Cu-Zn and Cu-Cr catalyst systems, various products were formed, the major product being citronellal, not citral.

b) The Effect of the Hydrogen Acceptor when Added to Reaction System. In the catalyzed dehydrogenation of geraniol, as will be described later, an equilibrium can be assumed between citral, citronellal, and geraniol in the reacting zone; it is reasonable to prevent the hydrogenating of citral into citronellal, and thereby increase the yield of citral, by using a hydrogen acceptor. Therefore, a hydrogen acceptor, such as ethylene, acetone or quinoline, was used. The results obtained are indicated in the columns for runs 4, 5 and 6 in Table 3. When acetone (1:1 by volume for geraniol) was used in the Cu-Zn catalyst system, the conversion of geraniol decreased and the formation of terpene hydrocarbons increased. When ethylene was used,⁶⁾ however, a decrease of a few percentage points in terpene hydrocarbons and an increase in citronellal from 37.8% (without hydrogen acceptor) to 45.2% were observed. When quinoline was used,⁸⁾ decreased yields of citral and citronellal were observed.

c) Contribution to the Hydrogenation of Hydrogen Molecules Adsorbed on the Catalyst. The product

distributions already shown for various systems suggest the possibility that citronellal and citronellol may be formed by the hydrogenation of citral and citronellal, respectively. Therefore, the contribution of the adsorbed hydrogen molecules to the hydrogenation was examined in the system of citral and a catalysts pretreated with hydrogen in a stream of nitrogen or of nitrogen mixed with hydrogen (10:1 by volume). As may be seen in columns 7 and 8 in Table 3, citronellol was not formed, while a comparable amount of citronellal was formed. The fact that no geraniol was made in this system can be explained; in view of the polarographic redox potentials corresponding to the reduction of citral into citronellal or geraniol,¹⁰⁾ it is reasonable to consider that geraniol, formed first, is then dehydrogenated into citronellal.

Liquid-phase Dehydrogenation. Liquid-phase dehydrogenation as well as vapor-phase dehydrogenation is a conveniently available method for preparing citral from geraniol, not only at the laboratory but also at the plant.

When using a Cu-Zn or Cu-Cr catalyst (2% by weight of the geraniol used the dehydrogenation should be carried out in a flask under gentle boiling between 200°C and 205°C; below this temperature, for example, at 180°C, the reaction is slow and inefficient.

In a comparison of the catalytic activity of Cu-Zn and Cu-Cr catalysts, it is evident that the latter catalyst gives terpene hydrocarbons and decreased yields of both citronellal and isopulegol (see runs 2 and 3 in Table 4).

To increase the yield of citral by preventing the conversion of the once-formed citral into citronellal, either citronellal or cyclohexanone, as a hydrogen acceptor, was added at the beginning of the reaction. From the results shown in Table 4 for the system with a Cu-Zn catalyst, when citronellal or cyclohexanone was used, the reaction resulted in a relatively increased yield of citral for the converted geraniol, the yield being even larger than that obtained in the vapor-phase dehydrogenation at an atmospheric pressure. Moreover, a larger amount of isopulegol was formed in the

TABLE 5. EFFECT OF REACTION TEMPERATURE ON PRODUCT DISTRIBUTION AT REDUCED PRESSURE IN VAPOR-PHASE DEHYDROGENATION USING Cu-Zn CATALYST*

Run	Volume of catalyst ml	L.S.V. l/hr	Reduced pressure mmHg	Temperature °C	Composition of products by G.L.C. (wt%)				
					Terpene hydrocarbons	Citronellal	Isopulegol	Citral	Geraniol
1	10	0.7	8	175	6.7	48.4	4.1	28.6	12.2
2	10	0.7	8	190	6.0	36.5	4.0	23.7	29.8
3	10	0.7	8	215	6.0	34.0	3.2	30.0	26.8
4	10	0.7	8	230	6.3	32.1	2.9	37.9	20.8

* Form of the catalyst used was of (b).

10) K. Schwarbe, G. Ohloff and H. Berg, *Z. Elektrochem.*, **57**, 293 (1953).

TABLE 6. EFFECT OF CONTACT TIME ON PRODUCT DISTRIBUTION AT A REDUCED PRESSURE IN VAPOR-PHASE DEHYDROGENATION USING Cu-Zn CATALYST SYSTEM

Run	Volume of catalyst* ml	Reaction temperature °C	L.S.V. t/hr	Reduced pressure mmHg	1/S.V. sec	Terpene hydrocarbons	Citronellal	Isopulegol	Citral	Geraniol	Citronellol
1	30	230	0.7	7	6.27×10^{-3}	6.2	15.7	5.2	48.0	24.9	0
2	30	230	0.7	21	18.7×10^{-3}	10.1	18.1	6.5	43.9	21.3	0
3	30	230	0.7	30	26.8×10^{-3}	8.4	19.0	6.6	47.7	18.3	0
4	30	230	0.7	42	37.4×10^{-3}	6.5	20.1	7.0	51.4	15.0	0

Table 5 The effect of contact time on the product distribution in the vapor phase dehydrogenation with the Cu-Zn system.

* Form of the catalyst was (b).

TABLE 7. VARIATIONS OF INVERSE RELATION OF CITRAL AND CITRONELLAL FORMATION *versus* REACTION TIME

Run	Sampling time	Cu-Zn* catalyst ml	Reaction temperature	L.S.V.	Reduced pressure mmHg	Compositions of products by G.L.C. (wt%)					Yield of citral plus citronellal (%)
						Terpene hydrocarbons	Citronellal	Isopulegol	Citral	Geraniol	
1	after 1 hr	35	185°C	0.7	15-16	7.0	71.3	0	21.5	0	92
2	after 5 hr	35	185°C	0.7	15-16	7.0	67.7	0	25.2	0	92
3	after 8 hr	35	185°C	0.7	15-16	7.1	63.3	0	27.6	2.0	90

* Form of the catalyst was (c).

TABLE 8. EFFECT OF CITRONELLAL ADDITION ON THE YIELD OF CITRAL USING Cu-Zn CATALYST

Run	Volume of catalyst* ml	Reaction temperature	Reduced pressure mmHg	L.S.V.	Molar ratio of geraniol to citronellal added	Composition of products by G.L.C. (wt%)					Geraniol conversion to citral (%)
						Terpene hydrocarbons	Citronellal	Isopulegol	Citral	Geraniol	
1	30	230°C	8	0.7	1:0.5**	2.0	48.5	5.9	43.4	0.2	65.3
2	30	230°C	8	0.7	1:1**	2.0	53.7	6.0	35.5	1.8	75.0
3	30	230°C	8	0.7	1:1.3**	1.2	57.5	5.2	34.9	1.2	84.0
cf	30	230°C	7	0.7	only geraniol	6.2	15.7	5.2	48.0	24.9	63.9

** The composition of these mixture used was, e.g., terpene hydrocarbons : citronellal : geraniol = 0.5 : 32.9 : 66.6 for Run 1, 0.5 : 32.9 : 66.6 for Run 2, and 0.8 : 59.4 : 41.8 for Run 3.

* Form of the catalyst used was of (c).

addition of citronellal than in that of cyclohexanone, indicating the transformation of citronellal into isopulegol.

Vapor-phase Dehydrogenation of Geraniol at Reduced Pressure. The fact that citral, as is shown in runs 7 and 8 in Table 3, gave various products, such as terpene hydrocarbons, citronellal and isopulegol, suggests the possibility of increasing the yield of citral by quickly removing the citral formed from the reacting zone. Therefore, the vapor phase dehydrogenation of geraniol was attempted with the Cu-Zn catalyst system at a reduced pressure and at a given L. S. V.; the results are summarized in Table 5.

a) *The Effect of the Reaction Temperature at a Given L. S. V.* The effect of the reaction temperature on the product distribution was examined between 175°C and 230°C and at a L. S. V. of 0.7, using a reaction tube packed with 10 ml of the catalyst (b), the results obtained are presented in Table 5. At the lower temperature, 175°C, citral decreased and citronellal increased markedly, reaching a yield of 48.4% after 7 ml of geraniol had been passed through in 1 hr, with the raising of the reaction temperature, the amount of citral increased, while that of citronellal, in turn, gradually decreased. In addition, an appreciably decreased conversion of geraniol was found in this system in comparison with that in dehydrogenation under an atmospheric pressure.

b) *The Effect of L. S. V.* The product distribution when 30 ml of the Cu-Zn catalyst (b) was used was examined at the most favorable reaction temperature, 230°C, with various contact times, the results obtained are summarized in Table 6. In this system, it will be noted that in comparison with the systems previously studied, there was an appreciably improved yield of citral (50%), a smaller amount of by-products, and no citronellol. In this case, the geraniol conversion *versus* the contact time shows a linear relation, as is shown in Fig. 2. This indicates, by extrapolation, that the complete conversion of geraniol would be ap-

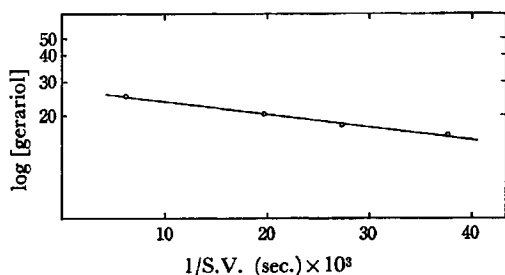


Fig. 2. Linear relationship between logarithm of geraniol molar concentration and contact time at 230°C in catalytic dehydrogenation using Cu-Zn catalyst.

proximately 60% under the present conditions.

c) *The Effect of the Addition of Citronellal.* In the results of the detailed observation of the product distribution shown in Table 7, it will be noted that the relation of the amounts of citral and citronellal is inverse, in that one increases as the other decreases, suggesting the possibility of these existing an equilibrium relation between citral, citronellal, and geraniol in this reacting zone, or of their changing the catalytic activity, controlling the equilibrium between them.

On the basis of the above reasoning, for the purpose of increasing the yield of citral, the present authors conducted the dehydrogenation at a reduced pressure by using mixtures of geraniol and citronellal in various ratios as the starting material.

As may be seen in the results shown in Table 8, the expected increased conversion of geraniol into citral was observed, while a maximum yield of citral of 84.0% was obtained.

The Preparation of Citronellal. It has already been demonstrated that the yield of citronellal was greatly affected by both the contact time and the reaction temperature. Therefore, in order to increase the yield of citronellal, the dehydrogenation of geraniol was carried out with a longer reaction tube and at a lower reaction temperature; the reaction temperature was 185°C, the reduced pressure 15 to 16 mmHg, and a reaction tube 28 mm in dia., 400 mm long, and packed with 35 ml of the catalyst (c) over a distance of 70 mm, was used. The results obtained are shown in Table 7. There was an excellent yield of citronellal (70%), but no formation of either isopulegol or citronellol.

A Proposal for the Catalyzed Dehydrogenation of Geraniol. On the basis of the dehydrogenation products already revealed, the following reaction process may be considered. Citronellal is formed by the hydrogenation of citral, not with hydrogen adsorbed on the catalyst, but with hydrogen participating in the dehydrogenation of geraniol. Such an example has been shown by Constable¹¹⁾ in the catalyzed dehydrogenation of allyl alcohol,¹²⁾ where propionaldehyde, not acrolein, is formed as a result of hydrogen migration from the alcohol to the carbon-carbon double bond of the possibly-made acrolein.

Regarding citral, judging from its increased yield upon the addition of citronellal, there is the possibility of an equilibrium relation between citral, citronellal, and geraniol in the reacting zone, or a poisoning of the catalyst, thereby resulting in a selectivity in the making of citral.

11) F. H. Constable, *Roy. Soc. Proc.*, **109**, 254 (1926).

12) D. E. Weston and H. Adkins, *J. Am. Chem. Soc.*, **50**, 1930 (1928).