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Thermal Decarbonylation of Tropone[1)]

Akira Amano, Toshio Mukai,* Tomoo Nakazawa,*,** and Kiyoaki Okayama*,***
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aoba-Aramaki, Sendai 980
**Department of Chemistry, Faculty of Science, Tohoku University, Aoba-Aramaki, Sendai 980*
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Thermal reaction of tropone has been studied at temperatures ranging from 420 to 490 °C and at residence times ranging from 1.5 to 6.9 s using a conventional flow apparatus. Tropone undergoes first-order unimolecular decarbonylation. The value of kinetic parameters for this reaction are evaluated as being: $A=10^{14.2}$ s^{-1}, $E_a=54.1$ kcal mol^{-1}, $\Delta S^{\ddagger}=2.8$ eu, $\Delta H^{\ddagger}=52.6$ kcal mol^{-1}, and $\Delta G^{\ddagger}=50.6$ kcal mol^{-1}. These values indicate that the decarbonylation takes place by one-step concerted mechanism *via* a norcaradienone-like transition complex. The latter complex is characterized by a partial transannular C_2–C_7 bond formation and concerted elongation of C_1–C_2 and C_1–C_7 bonds in tropone. The proposed transition complex is in conformity with reported thermal behavior of 1,3,5-cycloheptatriene as well as with molecular orbital symmetry theory.

A considerable attention has been directed to the pyrolysis of seven-membered conjugate systems. They include 1,3,5-cycloheptatriene,[2)] 7,7-dicyanonorcaradiene,[3)] 7-cyano-7-(trifluoromethyl)norcaradiene,[3)] 7,7-dimethoxycycloheptatriene,[4)] tropone ethylene acetal,[5)] thiepine derivatives,[6)] thiepine 1,1-dioxide,[7)] and azepine.[8)]

Concerning thermal reactivities of troponoid compounds, Dauben and his coworkers suggested in 1960 on the basis of their mass-spectroscopic observation that in the pyrolysis of 7-methoxycycloheptatriene benzene and carbon monoxide could be produced through an intermediary formation of tropone.[9)] It was supposed along with Woodward-Hoffmann Rule[10)] that the troponoid compounds exhibited the behavior to heat different from that to photoirradiation, on which bicyclo[3.2.0]hepta-3,6-dien-2-ones were formed.[11)] As our expectation, we have found quite unique, thermally induced rearrangements of troponoid compounds such as quantitative decarbonylation of tropone and comprehensive transformation of tropones and tropolones leading to benzenoid compounds.[1,12)] It has been expected then that further investigations on this novel reaction would provide with valuable informations as to norcaradiene skeleton frequently assumed but still controversial intermediate for the reactions of seven-membered conjugate system. The investigations should also be reckoned important, since the reaction may serve as an example of the thermal reaction of seven-membered compounds to test molecular orbital theory advanced by Woodward and Hoffmann.[10)] This paper deals with the kinetics for the decarbonylation reaction of tropone in details.

Experimental

Materials. Tropone of sufficient purity for use with the present kinetic measurements was prepared from an authentic sample of tropone picrate (mp 99—100 °C, yellow needles). The picrate was treated with aqueous ammonia and tropone was extracted with chloroform. After the extract was washed with water and dried over anhydrous sodium sulfate, chloroform was evaporated off from the extract and the residual oil was distilled at 80 °C under 5 mmHg. Gas chromatographic analysis of the distillate revealed no evidence of contamination of tropone. Toluene used as solvent was of reagent grade and of not less than 99.95 mol% purity. Cylinder helium used as carrier gas was of not less than 99.9 mol% purity. Both of these were used as received.

Kinetic Measurements. Toluene carrier technique was employed using a conventional all-glass flow apparatus. A touelne solution of 11.04 mol% tropone was introduced into the apparatus from a glass syringe of 19.3 mm in inside diameter. Reaction vessel was made of a quartz tubing, 20 mm in inside diameter and 140 mm in length, and was equipped with a thermo-sheath placed along its central axis. The vessel was fitted in an electrically heated aluminum-bronze block furnace, the temperature of which was controlled electronically within ±0.1°. Temperature profiles of the reaction vessel were determined, during each run while the reaction was taking place, by a movable Pt-Pt·Rh thermocouple in the sheath. Annular space of the vessel was filled with quartz tips, leaving a free volume of 14.30 ml. Injection of the solution was maintained at a rate of 20.75 ml·min^{-1} by a microfeeder to which the syringe was mounted. The tropone-toluene vapor was then carried into the reaction vessel along with a stream of helium dried over magnesium perchlorate. Rate of the latter stream, varying from 16 to 90 ml·min^{-1} (STP), was controlled by a needle valve and was measured by a soap-film flow meter within ±0.5%. Tropone in the reaction vessel was thus doubly diluted both by toluene and by helium that the pressure of tropone was kept below 30 mmHg throughout the present investigation. The pressure limitation such as described above was found important to eliminate carbonaceous materials formed otherwise. The reaction was carried out under conditions varied over the following ranges: temperature, 420—490°; residence time, 1.5—6.9 s. Product gases were passed through a train of traps, chilled by ice and methanol–Dry Ice, in which condensable components were collected for analysis. Non-condensable components were first led to a gas sampling tube immersed in liquid nitrogen to separate carbon monoxide, and were then purged after measurements of their flow velocities.

Definition of Temperature and Residence Time. From the observed temperature profiles of the reaction vessel, the following approximation was found valid. Where z is the length in mm along the reactor axis and other symbols

$$\int_{z=0}^{z=140} \exp(-E/RT)\,\mathrm{d}z \approx \int_{z=20}^{z=100} \exp(-E/RT)\mathrm{d}z$$

** Present address, Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560.

*** Present address, Yokkaichi Work, Mitsubishi Petrochemical Co. Yokkaichi, Mie 510.

have their usual significances. Effective reactor length was therefore 80 mm, corresponding to an effective reactor volume, V, of 8.17 ml. The average reaction temperature, T_{av} could then be defined by a graphic integration according to the following equation. The value of activation energy,

$$T_{av} = \frac{2.303E}{R}\log\left\{\int_{z=20}^{z=100}\exp(-E/RT)\mathrm{d}z/80\right\}$$

E, used with the above equation should coincide with the resulting value, E_a, determined from temperature dependence of specific reaction rate. This match was attained by trial-and-error calculations. Residence time, t, in s was calculat-

$$t = PVT/760\ T_{av}F$$

ed by the equation, where F is the corrected total flow rate of the reactant gas mixture in ml s^{-1}, T the room temperature, and P the atmospheric pressure in mmHg.

Analysis. Condensable components collected in the traps, consisting of benzene, toluene and unreacted tropone, were analyzed gas chromatographically using a combined column composed of 3 m Thermol-3 and 3 m Silicone Grease DC-550 at 150° with 40 ml min^{-1} of helium as a carrier gas. Under the given conditions, retention volumes were: benzene, 352 ml; toluene, 456 ml. Error involved in the analysis was estimated to be approximately ±2% of recorded values. Carbon monoxide collected in the gas sampling tube was also analyzed by gaschromatograph using a 5 m Molecular Sieve 5A column at 0° with 40 ml min^{-1} of helium as a carrier gas. In a few runs, results obtained by the gas-chromatographic analysis were confirmed by a mass-spectrographic analysis.

Results

Thermal Reaction of Tropone and the Related Compounds. Threshold temperature of tropone pyrolysis was found to be approximately 400°C, and as will be shown later the rate of the reaction could be most conveniently measured at temperatures between 420 and 500 °C. Besides tropone unreacted and toluene used as solvent, the pyrolyzates were consisted exclusively of benzene and carbon monoxide. Neither polymerization nor condensation products were detected both in the pyrolyzates and on the wall of the reaction vessel. Analysis of the products revealed that the amount of benzene was consistently in equi-molar with that of carbon monoxide. Therefore the reaction can be characterized simply by the following stoichiometry:

Tropone → Benzene + Carbon Monoxide

In a few preliminary runs, however, a considerable amount of biphenyl was formed at temperatures exceeding 800°. Since an entirely different principle may operate in the pyrolysis at extremely high temperatures, the biphenyl forming reaction will be ignored in our present discussion.

Order and Molecularity of the Reaction. Summarized in Table 1 are the results of twenty-six kinetic measurements carried out under the specified conditions. In each of these runs, conversion of tropone was kept below 25% and was usually in the range of 1—15%. This precaution was taken to avoid data which were inadequate for use with the following kinetic analysis. Illustrated in Fig. 1 are the plots of $-\log(1-x)$ *vs.* t, where x denotes fraction of tropone consumed. With exceptions of runs where conversions were higher, experimental data are all fitted with well-defined straight line passing the origin. The reaction is, therefore, first order in tropone with no induction period. These together with the fact that bibenzyl

TABLE 1. PYROLYSIS OF TROPONE

Temperature (K)	Residence time (s)	Conversion (mol%) × 10^3	Rate constant (s^{-1})
691.6	4.11	0.42	1.027
692.0	3.66	0.30	0.819
696.0	5.02	0.57	1.160
709.2	5.27	2.28	4.391
711.6	6.60	2.55	3.904
714.5	6.02	2.73	4.589
715.6	3.07	1.66	5.453
733.0	2.92	3.92	13.69
733.0	3.77	4.98	13.56
733.0	4.78	5.59	12.03
734.0	5.13	6.81	13.75
734.0	6.32	8.08	13.33
734.0	7.49	12.31	17.53
734.0	8.91	14.35	17.63
739.6	5.98	11.47	34.59
745.0	2.99	7.61	26.51
745.0	4.55	10.26	23.78
745.3	3.82	8.47	23.16
745.4	2.02	4.77	24.17
745.4	8.97	17.33	21.22
746.1	5.93	13.84	25.11
750.0	2.25	8.78	40.86
750.4	3.39	8.36	25.73
754.3	5.73	15.50	29.38
754.6	6.59	25.65	44.98
756.7	4.73	12.55	28.36

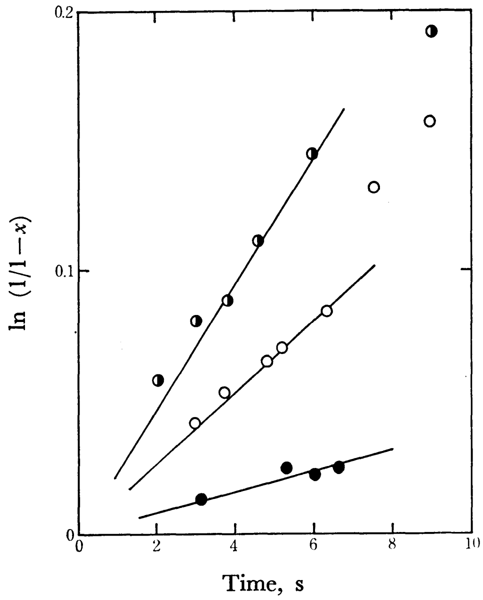

Fig. 1. First-order plots for the decarbonylation of tropone. Filled circles, 438 °C; half-filled circles, 472 °C; empty circles, 461 °C.

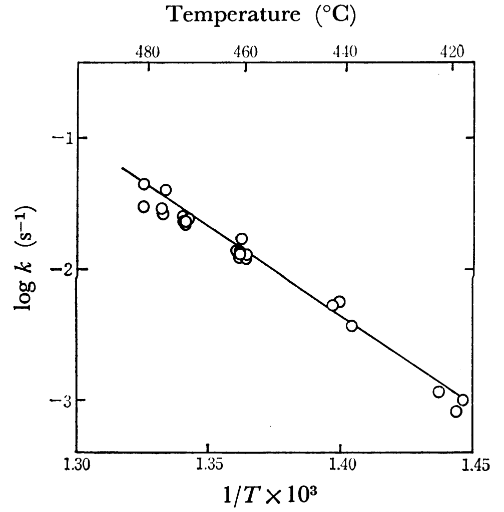

Fig. 2. Arrhenius plots for the decarbonylation of tropone.

Table 2. Rate constants

Temperature (K)	Rate constant $\times 10^3$ (s^{-1})
711.6	4.2 ± 0.27
734.0	13.4 ± 0.93
745.4	23.6 ± 0.80
754.6	41.7 ± 5.5

was not formed would strongly suggest that the decarbonylation takes place *via* a simple unimolecular splitting off of carbonyl group.

Kinetic Parameters. Listed in Table 2 are the values of rate constant calculated from the slope of the lines in Fig. 1. Error limits, estimated from uncertainties involved in measured quantities, are also indicated for each value of the rate constants. Arrhenius plots based on the values listed in the table are given in Fig. 2. Thus, rate constant can be expressed by the following equation:

$$\log k(\mathrm{s}^{-1}) = (14.22 \pm 0.67) - (54100 \pm 2000)/4.575\,T$$

Thermodynamic properties of the transition complex can therefore be characterized by the following values: $\Delta S^{\neq} = 2.8 \pm 3.0$ eu, $\Delta H^{\neq} = 52.6 \pm 2$ kcal·mol⁻¹, and $\Delta G^{\neq} = 50.6 \pm 2$ kcal·mol⁻¹.

Discussion

Mechanism of Decarbonylation. Illustrated in Fig. 3 are feasible pathways through which tropone may undergo unimolecular decarbonylation.

Of the three paths, Path A, proposed for the reaction of 2-azidotropone,[13] can be ruled out for the present case in view of strong C_1–C_2 linkage. Recent investigations on tropone by use of X-ray analysis,[14] gas phase electron diffraction,[15] NMR spectroscopy, [16,17d] and on the basis of theoretical calculations[17] reveal its structure, as being planar, with pronounced bond alternation. Dipole moment of 4.17—4.30 D reported for tropone,[18] exhibits, along with the presence of carbonyl stretching band in lower frequency region,[19] π-stabilization to a considerable extent.[20] The stabilization energy for tropone measured from the heat of hydrogenation is higher than that for nonplanar cycloheptatriene[21,22] by 3 kcal mol⁻¹. All these structural evidences definitely indicate that the energy required for α-cleavage of tropone ring is no less than 78 kcal·mol⁻¹, the value usually assigned for $D(CH_3CO\text{-}CH_3)$ in acetone.[23] The value of $E_a \approx 54$ kcal·mol⁻¹ observed in the present work is too low for the decarbonylation to take place *via* Path A. The value of $\Delta S^{\neq} \approx 2.8$ eu observed is also incompatible with this path. Biradical formation would remove restrictions of internal motions, resulting in an increase of entropy by a considerable amount. The argument is quite similar to that given for the isomerization of cyclobutenes.[24] In this latter case, experimentally observed value of $\Delta S^{\neq} \approx -0.7$ eu was taken as an evidence against the biradical mechanism. Mention should also be made of the fact that bibenzyl was not detected in the present work.

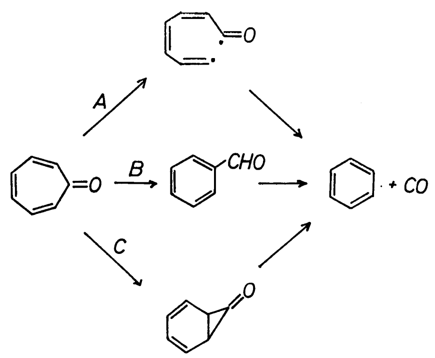

Fig. 3. Mechanism for the decarbonylation of tropone.

Intermediary formation of benzaldehyde *via* α-cleavage concerted with hydrogen atom migration is assumed in Path B. The assumption is based on a somewhat superficial interpretation of the reactions of a similar type such as isomerizations of cycloheptatriene[2] and 2-chlorotropone.[12] This path is clearly ruled out on the following experimental grounds. According to our preliminary examinations, benzaldehyde was not detected in the pyrolyzates and benzene was not formed from benzaldehyde under conditions comparable with those in the present work.

Only Path C is now left for consideration. As will be seen later, it is concluded in our present discussion that Path C with slight modification is in accord with a bulk of the latest informations. Since norcaradienone assumed in this path bears an intimate relation with norcaradiene intermediate in the isomerization of cycloheptatriene, the mechanism *via* Path C will be discussed separately in the subsequent paragraph with special reference to that of the latter compound.

Norcaradiene Skeleton as Transient Structure. As has been mentioned earlier, cycloheptatriene isomerizes to the corresponding benzene derivatives at temperatures around 100 °C.[2] The values of kinetic parameters have been assigned as being $E_a \approx 51$ kcal mol⁻¹ and $A \approx 10^{13.5}$ s⁻¹. The reaction, therefore, takes place

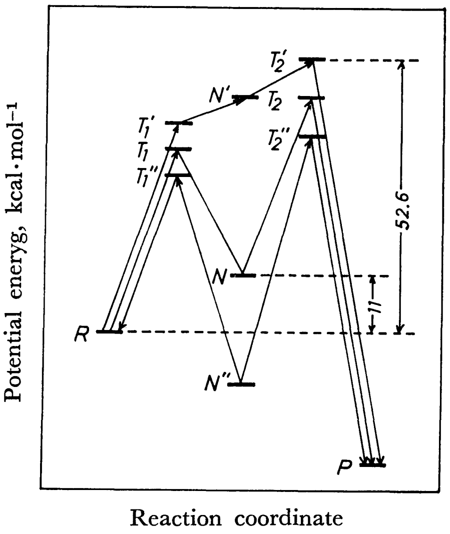

Fig. 4. Potential energy diagram for reactions involving norcaradiene skeleton.

at a rate comparable with that of tropone. Klump and Chesick discussed the reaction in terms of a metastable norcaradiene intermediate in equilibrium with cycloheptatriene.[2b)] Energetics of the Klump-Chesick mechanism can best be expressed by the steps, $R \rightarrow T_1 \rightarrow N \rightarrow T_2 \rightarrow P$, illustrated in Fig. 4. In this figure, R, P and N (also N′ and N″) represent energy levels of reactant, product and transient complex having norcaradiene skeleton, respectively. Those of the first and the second transition-states are also represented by T_1 and T_2 (also T_1', T_1'', T_2' and T_2''). Although mechanistic similarity does exist between the pyrolyses of cycloheptatriene and tropone as to the tendency toward the formation of norcaradiene skeletone, norcaradienone formed from tropone is believed to be far less stable than norcaradiene assumed in the Klump-Chesick mechanism.

Referred to below are some indirect evidences in support of the above statement. Valence isomerization between the cycloheptatrienes and norcaradienes has been extensively studied[25)] and many norcaradiene derivatives were found to exist even at room temperatures.[3,26)] Norcaradiene in equilibrium with cycloheptatriene has never been observed spectroscopically but the Diels-Alder reaction of cycloheptatriene with dienophiles such as maleic anhydride affords an adduct derived from norcaradiene as an only product.[27)] Contrary to these, an isolation of norcaradienone has never been documented and there is no evidence for its existence. The Diels-Alder reaction of tropone gives rise not to an adduct derived from norcaradienone but to that obtained by direct addition to 2 and 5 positions of tropone nucleus.[28)] Furthermore, higher reactivity found in cyclopropanone which undergoes ring opening quite readily[29)] and the higher π-stabilization found in planar tropone than that in nonplanar cycloheptatriene[21,30)] suggest that the process from tropone to norcaradienone is energetically less favorable than that from cycloheptatriene to norcaradiene. Thus, for the case of tropone, N in Fig. 4 would be raised to N′, and consequently T_1 to T_1' and T_2 to T_2'. The reaction now takes place through Path C comprizing the steps: $R \rightarrow T_1' \rightarrow N' \rightarrow T_2' \rightarrow P$. The level N′ no longer stands for an intermeidate in its usual terminology, but is more like a transient complex between two transition-states. The assumption of such norcaradienone-like complex does not conflict with the observed normal A-factor and moderate E_a value. Steric course of the proposed mechanism will be discussed in more detail on the light of the rule advanced by Woodward and Hoffmann.[10)]

Table 3. Symmetry of HOMO and LVMO of tropone

Orbital numbers	1	2	3	4	5	6	7	8
HOMO	−	+	+	−	−	+	+	−
LVMO	0	+	−	−	+	+	−	0

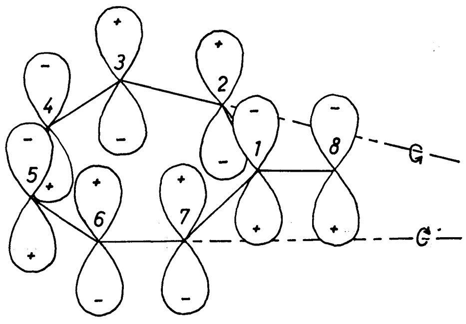

Fig. 5. Orbital symmetry and steric course for the decarbonylation of tropone.

It should be mentioned that 7,7-dicyanonorcaradiene and 7-cyano-7-(trifluoromethyl)norcaradiene have been recognized in stable form.[3)] In these compounds, electrophilic substituents on C_7 must have strong stabilization effect toward norcaradiene.[31)] The net effect in this case is, therefore, to lower the intermediate level from N to N″, and hence the transition-state levels from T_1 and T_2 to T_1'' and T_2'', respectively. The isomerization would then take place in two ways: $N'' \rightarrow T_1'' \rightarrow R$ and $N'' \rightarrow T_2'' \rightarrow P$. Results obtained by Giganek support this view.

Molecular Orbital Symmetry Theory. Molecular orbital symmetry theory provides a clear-cut account for stereochemical consequences observed in thermal as well as photochemical valence isomerizations of polyolefins.[10)] The decarbonylation of tropone appears to be a newer addition to those for which this theory is obeyed. Listed in Table 3 are the reported symmetry factors of the highest occupied and the lowest vacant molecular orbitals of tropone.[32)] For thermal reactions where HOMO determines the steric course, the theory predicts the overlap between orbitals of the C_2 and C_7 positions by disrotatory process as illustrated in Fig. 5. As the C_2–C_3 and C_6–C_7 bonds rotate in the directions indicated by curved arrows in Fig. 5, a partial bond is formed between the C_2 and C_7 positions, and carbonyl group is squeezed out from the plane of the ring. This can only take place at the expense of the weakening of the C_1–C_2 and C_1–C_7 bonds. The compensation described above as to the rigidity of the molecule as a whole is in conformity with the small value of $\Delta S^{\neq}$ 2.8 eu observed in the present study. The resulting structure is identical with the norcaradienone-like transient complex brought up earlier in connection with Path C.

In sharp contrast with thermally induced reactions, photolysis of tropones has been known to form $\Delta^{3,6}$-bicyclo[3.2.0]hepta-3,6-dien-1-one.[11] Since the steric course of photochemical reactions is determined by the symmetry of LVMO, the photolyzate of tropones is again in conformity with the theory. Thus, it appears that the molecular orbital symmetry theory can be extended to cover reactions of seven-membered conjugate system at elevated temperatures.

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