H-14 signals were observed at δ 6.00 and 7.60, respectively, with $J_{11,14} = 1.0$ Hz.



 C_{16} terpenoids appear to be unique in nature, and the isolation of I and II raises interesting biogenetic questions. Inspection of structure I suggests a possible origin from a C_{20} precursor by microbiological degradation although one might also consider derivation from a C_{15} precursor (XI) by the addition of a C_1 unit to C-11.



George A. Ellestad, Ralph H. Evans, Jr. Martin P. Kunstmann Lederle Laboratories A Division of American Cyanamid Company Pearl River, New York 10965 Received February 12, 1969

Equilibrium Constant for Allyl Radical Recombination. Direct Measurement of "Allyl Resonance Energy"

Sir:

We report the direct measurement of the equilibrium constant, $K_{r,d}$, for reaction 1 and, thereby, a direct measurement of the allyl resonance energy (ARE).¹

$$M + 2allyl \stackrel{kr}{\underset{kd}{\longrightarrow}} 1,5-hexadiene + M \tag{1}$$

Values of $K_{r,d}$ have been determined at 913 and 1063 °K (Table I), and these, combined with the known entropy change (Tables I and II) for the reaction, yield

Table I. Experimental Results

	913°K	1063°K		
$k_{\rm d}$, sec ⁻¹	4.3	5.5×10^{2}		
$k_{\rm r}, M^{-1} {\rm sec^{-1}}$	$7.4 imes 10^{9}$	$5.0 imes 10^9$		
$K_{\rm r,d} M^{-1}$	1.8×10^{9}	9.4×10^{6}		
$\Delta S^{\circ}_{r,d}$ gibbs/mol ^a	-34.8	-34.7		
ΔE° , kcal/mol ^b	-61.0	- 59.5		
ΔH° , kcal/mol	-62.8	-61.6		

^a Table II. ^b ln $K_{r,d}$ $(M^{-1}) = [\Delta S^{\circ} - \Delta nR(1 + \ln (R'T))]/R$ - $(\Delta E^{\circ}/RT)$, where the superscript refers to a standard state of 1 atm and R' distinguishes the gas constant in units of 1.-atm/mol °K from units of cal/mol °K.

(1) Defining the bond dissociation energy (BDE) for any bond A-B $DH^{\circ}_{T}(A-B) = \Delta H^{\circ}_{\mathfrak{f},T}(A) + \Delta H^{\circ}_{\mathfrak{f},T}(B) + \Delta H^{\circ}_{\mathfrak{f},T}(AB)$

we may define the stabilization energy in the allyl radical, commonly called the allyl resonance energy (ARE), as

$$DH^{\circ}_{298}(n-C_{3}H_{7}-H) - DH^{\circ}_{298}(allyl-H) \equiv ARE$$

a value of the enthalpy change which, corrected to room temperature (Table II), is $\Delta H^{\circ}_{r,d} = -62.2$ kcal/mol. Since

$$\Delta H^{\circ}_{r,d}(T^{\circ}K) = \Delta H^{\circ}_{f,T}(BA) - 2\Delta H^{\circ}_{f,T}(A)$$
(2)

and since $\Delta H^{\circ}_{f,298}(BA) = 20.2 \text{ kcal/mol}$ (Table II), this leads to $\Delta H^{\circ}_{f, 198}(A) = 41.2 \text{ kcal/mol.}$

Table II. Thermochemical Quantities

Molecule	$\Delta H^{\circ}{}_{\mathrm{f},298}{}^{a}$	$S^{\circ_{298}b}$	$C^{\circ}{}_{{ m p},300}{}^{b}$	C° _{p.800} ^b	$C^{\circ}_{\rm p,1000}$	C°,,1500
1,5-Hexadiene⁰	$20.241.4\pm 1.1^{d}$	89.4	28.8	57.9	64.4	74.3
Allyl	41.2^{e}	62.1/	14.6/	28.8 ⁷	31.9 ⁷	36.8 ⁷

^a kcal/mol. ^b Gibbs/mol. ^c S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968; S. W. Benson, et al., Chem. Rev., in press. ^d Reference 3a [amended slightly by D. M. Golden and S. W. Benson, Chem. Rev., 69, 125 (1969); the original value was 40.6 kcal/mol]. • This work. We apologize for the fortuitous closeness of the two results. ¹ H. E. O'Neal and S. W. Benson, Int. J. Chem. Kin., 1, 217 (1969); ref c.

The above value of $\Delta H^{\circ}_{f,298}(A)$ yields $DH^{\circ}_{298}(allyl-H)$ = 88.4 kcal/mol, $DH^{\circ}_{298}(n-C_{3}H_{7}-H) = 98 \text{ kcal/mol};^{2}$ thus ARE = $9.6 \sim 10$ kcal/mol.

Controversy abounds as to the correct value of ARE. Values quoted range from 10 to 25 kcal/mol.³ The correct value is important, not only for knowledge of the BDE's of allyl-weakened bonds, but the actual numerical value must surely be fundamental for any theory which attempts to quantitatively describe chemical bonding.

Free-radical heats of formation are generally measured by kinetic methods. The difference between the activation energy in forward and reverse directions for any reaction involving the radical of interest will yield its heat of formation if the heats of formation of all the other species involved are known.

In practice, it has rarely been possible to measure activation energies in both directions, so that certain assumptions are made about the activation energy in a given direction. In ref 3a and 3b, E_3 is measured and the assumption is made that the activation energy $E_{-3} = 1 \pm 1$ kcal/mol when R is ally and methylally

$$RH + I \xrightarrow{3}_{-3} R + HI$$
 (3)

radical, respectively. In ref 3c-g, the measured rate constant is for homolytic bond scission and the assumption is that radical recombination, the back reaction, has zero activation energy.

Both assumptions seem to be reasonably well founded for simple alkyl radicals, but it has not been clear that they apply to allyl radicals. In addition, the bond

(2) J. A. Kerr, Chem. Rev., 66, 465 (1966).

⁽²⁾ J. A. Kerr, Chem. Rev., 66, 465 (1966). (3) See, for example: (a) D. M. Golden, A. S. Rodgers, and S. W. Benson, J. Am. Chem. Soc., 88, 3196 (1966); (b) K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, 86, 5420 (1964); (c) R. J. Akers and J. J. Throssel, Trans. Faraday Soc., 63, 124 (1967) [the value of $\Delta H^{\circ}_{1,298}$ -(allyl) quoted here is derived from an incorrect value of $\Delta H^{\circ}_{1,298}$ -(allyl) quoted here is derived from an incorrect value of $\Delta H^{\circ}_{1,198}$ -(allyl) and F. P. Lossing, Can. J. Chem., 44, 2211 (1966); (e) W. von E. Doering and V. Toscano, unpublished work [quoted by W. von E. Doering, et al., Tetrahedron, 23, 3943 (1967)]; (f) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1950, n. 50 (the value of ARE is referenced to $DH^{\circ}CH_{3}$ -H) = 102 1950, p 50 [the value of ARE is referenced to $DH^{\circ}(CH_{3}-H) = 102$ kcal/mol]; (g) J. A. Berson and E. J. Walsh, Jr., J. Am. Chem. Soc., 90, 4730 (1968).

scission reaction, being unimolecular, may be in the "fall-off" range when measured (see particulary ref 3d).

The unequivocal value of the heat of formation of allyl radicals is obtained from the third law enthalpy change for reaction 1. $K_{r,d}$ may be measured by determining equilibrium concentrations of A and BA, or by measuring both k_r and k_d under exactly⁴ the same reaction conditions. We have accomplished the latter by observing the decomposition of BA and of diallyl oxalate (DAO) in the same stirred-flow reactor VLPP⁵ apparatus. DAO decomposes to give 2A + $2CO_2$ and the A's combine to yield BA, the appearance of which is monitored at both 67 and 54 amu.

Table I shows the current results. Several items are especially noteworthy. First, $K_{r,d}$ has been determined at temperatures such that it varies by 200-fold in a manner consistent with the expected parameters. Second, although we expect the rate constants determined here to be below the high-pressure limit, the value of k_r is as high, or higher, than we expect the highpressure value to be.

The first point gives us some confidence in the results and the second may mean either that the high-pressure limit is attained or that there is some contribution from a heterogeneous recombination of allyl radicals. (The latter would not effect the value of $K_{r,d}$ since, of course, biallyl decomposition would be similarly affected.)

The value of 9.6 kcal/mol for ARE may be uncertain by as much as 2 or 3 kcal/mol, and this result will be refined with continued experiment, but it must surely lay to rest any thought that ARE is much greater than 12 kcal/mole!

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(4) Both k_r and k_d may or pressure dependent, but not their ratio, if k_r and k_d are determined under the same conditions. (5) S. W. Benson and G. N. Spokes, J. Am. Chem. Soc., 89, 2525

(1967).

(6) Postdoctoral research associate.

David M. Golden, Norman A. Gac,⁶ Sidney W. Benson Department of Thermochemistry and Chemical Kinetics Stanford Research Institute, Menlo Park, California 94025 Received January 8, 1969

Coordination and Transition Metal Catalyzed Ring Opening of Some Hydrocarbons Containing Condensed Cyclopropane Rings

Sir:

Previously¹ we have reported on the valence isomerization of exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) into tetra $cyclo[3.3.0.0^{2,8}.0^{4,6}]octane$ (2) in the presence of catalytic amounts of $Rh_2(CO)_4Cl_2$.

(1) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, J. Am. Chem. Soc., 91, 218 (1969).



The isomeric endo-tricyclo $[3.2.1.0^{2,4}]$ oct-6-ene (3) fails to undergo a similar reaction, which was attributed to the fact that the valence isomerization requires a simultaneous coordination of the hydrocarbon via the cyclopropane ring (edgewise) and the double bond.

In this communication we report on the interaction of other transition metal complexes with the hydrocarbons 1 and $exo_{,exo-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (4)$. We found that in the presence of catalytic amounts of IrCl(CO)(PPh₃)₂, 1 rearranges quantitatively to 5methylenebicyclo[2.2.1]hept-2-ene (5) upon heating at 130° in benzene. The ring opening was very selective;



no traces of 2 and of bicyclo[3.2.1]octa-2,6-diene (6) could be detected. Under similar conditions 4 rearranges to exo-6-methylenetricyclo[3.2.1.0^{2,4}]octane The structural assignment of 7 was based on its (7).



nmr spectrum which shows the characteristic pattern of an exo-fused cyclopropane ring² and the presence of two signals for the methylene group at 4.95 and 4.70 ppm (compare 5, 4.93 and 4.65 ppm from TMS).

Opening of the cyclopropane ring in 7 was not observed; the stability of 7 can again be ascribed to its inability to coordinate as a bidentate. For similar reasons, the endo isomer 3 and exo, endo-tetracyclo- $[3.3.1.0^{2,4}.0^{6,8}]$ octane (8)³ fail to react at 130° using IrCl(CO)(PPh₃)₂.



The thermal isomerization of 1 yields a different product. Compounds 1 and 4 are stable for at least 16 hr at 200°. Simmons reports that 1 is converted at 240° into tricyclo[3.2.1.0^{2,7}]oct-3-ene (9).⁵

(2) R. E. Pincock and J. Haywood-Farmer, Tetrahedron Letters, 4759 (1967).

(3) The hydrocarbons 1, 4, and 8 are prepared according to the (b) The hydrocarbons 1, 4, and 8 are prepared according to thm Simmons-Smith procedure⁴ and purified by preparative glpc. For nmr data of 1 and 4 see ref 1; nmr for 8 (ppm from TMS): H-1,5, 2.25, H-2,4, 0.70, H-3a, -0.08, H-3b, 0.32, H-6, 8,7a,7b, 1.25–1.47, H-9a, 0.95, H-9b, 0.59; $J_{2-3a} = 7.2$ cps, $J_{2-ab} = 3.2$ cps, $J_{3a-3b} = 6.5$ cps, $J_{6-2a} = 2.0$ cps, $J_{1-9a} = < 1.0$ cps, $J_{9a-9b} = 10.5$ cps. (4) S. D. Koch, R. M. Kliss, D. V. Lopiekes, and R. J. Wineman, J. Org. Chem. 26, 3122 (1961); H. E. Simmons and R. D. Smith, J. and Chem. Sec. 81, 4756 (1950)

(5) H. E. Simmons, quoted (in ref 15) by H. Prinzbach, W. Eberbach, M. Klaus, G, V. Veh, and U. Scheidegger, Tetrahedron Letters, 1681 (1966).

J. Am, Chem. Soc., 81, 4256 (1959).