tion). The products were separated by distillation and analyzed by gas-liquid chromatography and chromato-mass spectrometry. Mass spectrum of (IV), m/z (intensity, %): 40(79), 55(80), 69(80), 88(100), 96(41), 110(80), 152(37), 198 (10, M<sup>+</sup>).

#### CONCLUSIONS

A system containing  $WCl_6$  and 1,1,3,3-tetramethyl-1,3-disilacyclobutane catalyzes the metathesis of ethyl 4-pentenoic acid and its cometathesis with 1-heptene.

## LITERATURE CITED

- 1. A. Ellison, A.K. Coverdale, and P. F. Dearing, J. Mol. Catal., <u>28</u>, 141 (1985).
- 2. J. Levisalles and D. Villemin, Tetrahedron, 26, 3181 (1980).
- 3. N. S. Nametkin, V. M. Vdovin, and N. B. Bespalova, Dokl. Akad. Nauk SSSR, <u>225</u>, 577 (1975).
- 4. J. J. Ritter and T. Kaniecki, J. Org. Chem., <u>27</u>, 622 (1962).

# ENTHALPY OF FORMATION OF KETENE, ETHYNOL, AND THEIR ANALOGS

IN THE GAS PHASE

V. M. Orlov, A. A. Krivoruchko,

A. D. Misharev, and V. V. Takhistov

The reported enthalpies of formation for ketene in the gas phase range from -36.4 to -61.1 kJ/mole [1]. Taking the new value  $\Delta H_f^0(g)$  ( $CH_3C=O^+$ ) = 627.6 kJ/mole [2] and the proton affinity PA( $CH_2=C=O$ ) = 828.4 kJ/mole [1], we obtain  $\Delta H_f^0(g)$  = -74.1 kJ/mole. Our calculations based on  $\Delta H_f^0(g)$  (O=C=C=C=O) = -97.9 kJ/mole [3] give  $\Delta H_f^0$  ( $CH_2=C=O$ ) = -91.96 kJ/mole, while  $\Delta H_f^0$  (g) ( $CH_2=C=O$ ) = [ $\Delta H_f^0(O=C=O) + \Delta H_f^0(CH_2=C=CH_2)$ ]/2 = 101.3 kJ/mole. In order to determine the enthalpy of formation of ketene, we used a photoionization method which gives the ionization energy (IE) of molecules and appearance potential (AP) of fragment ions [4]. An attempt to obtain  $\Delta H_f^0(CH_2=C=O)$  from the fragmentation of acetanilide (IE = 8.20, AP [M - $CH_2=C=O$ ]<sup>+.</sup> = 9.74 eV) was unsuccessful since ion (I) whose enthalpy of formation is unknown was obtained rather than the expected ion, PhNH<sub>2</sub><sup>+</sup>.

UDC 536.722:547.387:547.362



The values  $\Delta H_{f}^{0}(g)(CH_{2}=C=0) = -87.24 \text{ kJ/mole was obtained upon the fragmentation of 3-phenylcyclobutanone (II) with IE + 8.83 and AP([PhCH=CH_{2})]^+) = 8.86 eV. Since the AP is virtually the same as the IE, the thermochemical threshold for the appearance of [M - CH_{2}=C=0]^+ may lie even lower since <math>\Delta H_{f}^{0}(g)$  (ChH\_{2}=C=0) < -87.24 kJ/mole, i.e., is significantly lower than the values proposed by Cox [3] (-61.1 kJ/mole) and, especially, by Benson [6] or in the review of Deming [6] (-47.7 kJ/mole).

The fragmentation of diketene (III) (IE = 9.53, AP  $[M - 42]^{+}$  = 10.98 eV) gives a very high value for  $\Delta H_{f^0} = +41.6 \text{ kJ/mole}$  for the neutral molecule with mass 42. The molecule may be the ketene isomer, ethynol HC=COH. Estimation of the IE of HC=COH give 9.7 eV for IE (CH<sub>2</sub>=C=O) = 9.61 eV [7], which is in accord with the scheme for the decomposition of (III) given above. Since the IE of tautomer (IV) should be significantly lower than the IE of (III) (9.53 kJ/mole)(for example, IE = 803 eV [7] for CH<sub>2</sub>=CHCH=CHOCH<sub>3</sub>), the isomzerization of (III) to (IV) is possible. Thus, we are the first to obtain an experimental value for  $\Delta H_f^0(g)$  (HC=COH) = +41.6 kJ/mole.

Institute of Molecular Biology, Academy of Sciences of the USSR, Moscow. Pharmaceutical Chemistry Institute, Leningrad. A. A. Zhdanov Leningrad State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2619-2621, November, 1986. Original article submitted April 16, 1986. Analysis of the enthalpies of formation of allenes [6] gives the following increments for  $C_A$  (the central atom in allene): 139.4 (allene), 14.51 (monosubstituted allene) and 144.9 kJ/mole (disubstituted allene), i.e., the introduction of two groups or a double bond (that is, cumulation) increases  $C_A$  by 6.5 kJ/mole. For the cumulated double bond attached to two carbon atoms bearing 0, S and N heteroatoms, we obtain  $C_A = 129.0$  kJ/mole starting from  $\Delta H_f^0(g)(C_3O_2) = -97.9$  kJ/mole and  $C_A = 136.9$  kJ/mole if there is only one heteroatom. The CO group in ketene has the increment -113.4 kJ/mole. Using the values obtained for the increment -106.9 kJ/mole (i.e.,  $-113.4 \pm 6.5$ ) kJ/mole. Using the values obtained for the enthalpies of formation of ketene, ethynol, increments for allenic carbon atoms, and increments for the substitution of =CO by =C=S and =C=NH and OH by SH and NH<sub>2</sub> at the double bond or in the benzene ring [3, 5, 8], we obtain the enthalpies of formation of the following unsaturated species (kJ/mole): O=C=C=O (-213.5),  $H_2C=C=S$  (167.4), HC=CSH (246.9), S=C=C=S (297.1), O=C=C=C=S (157.3), S=C=C=C=S (412.5),  $CH_3CHS$  (48.1),  $CH_2=NH$  (110.0),  $CH_3CH=$ NH (54.5), HN=C=NH (133.9), HN=C=C=NH (313.8),  $CH_2=C=NH$  (175.8),  $HC=CNH_2$  (221.8),  $CH_3CONH_2$ (-223.5) (instead of -241.8 [8]) and HNCO (-129.7) (instead of -92.5 kJ/mole [9]).

The value obtained for  $\Delta H_f^{0}(g)(0=C=C=0)$  (-213.5 kJ/mole) implies that the CO dimer is unstable relative to decomposition to two CO molecule ( $\Delta H_f^{0}(2CO) = -221.1 \text{ kJ/mole [5]}$ ). Since the CS dimer (S=C=C=S) is also not observed, this implies that  $\Delta H_f^{0}$  (CS) < 0.5  $H_f^{0}$  (C<sub>2</sub>S<sub>2</sub>)) (i.e., <148.5 kJ/mole). This leads to a new value for  $\Delta H_f^{0}(CS) \le 133.9 \text{ kJ/mole [11]}$  instead of 232.3 kJ/mole [3]. Since  $\Delta H_f^{0}(HNC:) = 178.2 \text{ kJ/mole [11]}$ , HN=C=C=NH ( $\Delta H_f^{0} = 313.8 \text{ kJ/mole}$ ) is stable relative to its decomposition into two NHC.

The enthalpies of formation were calculated according to the Benson scheme based on molecules with similar structure:  $\Delta H_f^0(II) = 22.8 \text{ kJ/mole}$  is obtained from  $\Delta H_f^0(CH_2CH_2CH_2CO) = -85.8 \text{ kJ/mole}$  [5] and  $\Delta H_f^0(III) = -174.6 \text{ kJ/mole}$  is obtained from  $\Delta H_f^0(CH_2CH_2CO) = -282.8 \text{ kJ/mole}$  and  $\Delta H_f^0(CH_2CH_2CH_2CH_2(H_2(29.15 [12]))$ . The value  $\Delta H_f^0(CH_2=CHOH) = -127.2 \text{ kJ/mole}$  was taken from the work of Siretskaya [13]. IE (HC=COH) = 9.7 eV was estimated from IE for  $CH_2=CHCH=CH_2$  (9.07 eV) and  $CH_2=CHOH$  (9.14 eV), PhCH=CH\_2 (8.47 eV), PhOH (8.50 eV) and HC=CCH=CH\_2 (9.58 eV) [7]. 3-Phenylcyclobutanone was obtained from PhCH\_2CO\_2H and  $CH_2N_2$ [14] and carefully purified through the bisulfite derivative to remove 2-phenylcyclobutanone. Commerical diketene was distilled prior to use.

## CONCLUSIONS

1. Enthalpies of formation were obtained:  $\Delta H_{f}^{0}(CH_{2}=C=0) \leq -87.24 \text{ kJ/mole}$  and  $\Delta H_{f}^{0}(HC=COH) = +41.6 \text{ kJ/mole}$ .

2. The enthalpies of formation of 13 ketene and ethynol analogs containing 0, N, and S atoms were calculated.

### LITERATURE CITED

- 1. S. G. Lias, J. F. Liebman, and R. D. Levin, J. Phys. Chem. Ref. Data, 13, 695 (1984).
- 2. R. Bombach, J.-P. Stadelmann, and J. Vogt, J. Chem. Phys., <u>72</u>, 259 (1982).
- 3. J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London (1970).
- 4. Y. A. Loguinov, V. V. Takhistov, and L. P. Vatlina, Org. Mass Spectrom., 16, 239 (1981).
- 5. S. W. Benson, Thermochemical Kinetics, Wiley-Interscience, New York (1976).
- 6. R. L. Deming and C. A. Wulff, in: The Chemistry of Ketenes, Allenes, and Related Compounds, S. Patai, ed., Wiley, Chichester (1980), p. 1.
- R. D. Levin and S. G. Lias, Ionization Potential and Appearance Potential Measurements 1971-1981, Ion Kinetics and Energetics Data Center, National Bureau of Standards, Washington (1982).
- 8. S. W. Benson, Chem. Rev., 78, 23 (1978).
- 9. B. J. Sullivan, G. P. Smith, and D. R. Crosley, Chem. Phys. Lett., <u>96</u>, 307 (1983).
- 10. M.-J. Hubin-Franskin, J. Katihabwa, and J. E. Collin, Int. J. Mass Spectrum. Ion Phys., 11. 20, 285 (1976).
- 12. A. G. Maki and R. L. Sams, J. Chem. Phys., 75, 4178 (1981).
- H. L. Finke, J. F. Messerly and S. H. Lee-Bechtold, J. Chem. Thermodyn., <u>13</u>, 345 (1981). 13. T. V. Siretskaya, Dissertation, Leningrad (1985).
- 14. L. T. Scott and M. A. Minton, Synthesis, No. 6, 411 (1977).