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Thermochemistry of organic, heteroorganic and inorganic species.The enthalpies of formation for halogenides of some A=B=C and A=B=C=D molecules.

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ABSTRACT

By application of empirical and semi-empirical methods the enthalpies of formation for series of XN=C=Y molecules (X = F, Cl, Br, I; Y = O, S, Se) were calculated. Empirical procedures was used for calculation of enthalpies of formation for X=C=C=X molecules with X = O, S, Se. The possibility of synthesis of carbon monoxide dimer O=C=C=O is discussed.

Key words: thermochemistry, heterocumulene systems, carbon monoxide dimer.

The present work continues our previous work on thermochemistry of ketene CH_2=C=O molecule and the related species of the A=B=C general structure [1] . In results of that work the enthalpy of formation for ketene molecule was drastically changed from currently used value -11.4 , *e.g.* see Ref. 2, to -24 kcal mol^{-1} [1] and the ΔH_f^0 values for some novel species of A=B=C series were derived, *e.g.* CH_2=S=CH_2, CH_2=S=S and S=S=S [1] . Here we consider a novel set of A=B=C-type species, namely, XN=CO and XN=CS molecules (X= F - I) and X=C=C=X (X = O, S, Se) which thermochemical data are unknown or conflicting.

We begin from analysis of ΔH_f^0 ClN=C=O molecule since for this one the set of experimental data is available > 52.9 [3] or 8.5 kcal mol^{-1} [4] . To derive ΔH_f^0 ClNCO we apply the enthalpic shift procedure originally suggested by Benson [5] , later applied to the thermochemistry of molecules by many authors, and finally formulated as a complete methodology for checking or correcting known and finding unknown values in our recent publications [6-9]. This time we analyze the known data for H → Cl enthalpic shift in molecules with H and Cl atoms attached to N-atom (Eqns 1-4) (ΔH_f^0 - kcal mol^{-1}):

$$\begin{array}{lccc} & \text{H-N=C=O} & \xrightarrow{>79.9} & \text{Cl-N=C=O} \\ \Delta H_f^0: & -27^2 & \Delta\Delta H_f^0 & >52.9^3 \end{array} \quad (1)$$

$$\begin{array}{lccc} & \text{H-N=C=O} & \xrightarrow{35.5} & \text{Cl-N=C=O} \\ \Delta H_f^0: & -27 & & 8.5^4 \end{array} \quad (2)$$

$$\begin{array}{lccc} & \text{H-N=C=O} & \xrightarrow{16} & \text{Cl-NH}_2 \\ \Delta H_f^0: & -11^3 & & 5^8 \end{array} \quad (3)$$

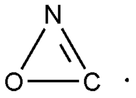
$$\begin{array}{lccc} & \text{H-N=C=O} & \xrightarrow{-11.4} & \text{Cl-N=O} \\ \Delta H_f^0: & 23.8^3 & & 12.4^{10} \end{array} \quad (4)$$

From Eqns 3 and 4 we see that H → Cl enthalpic shift depends on electronegativity (EN) of the substituent X. Applying the new EN scale [6] in which EN of F is assigned 10 units, we take EN values for NH_2-, NCO- and NO-groups 6.5, 7.9 and 8.5 units, respectively, and by interpolation gain $\Delta\Delta H_f^0$ for HN=C=O → ClN=C=O shift about -3 kcal mol^{-1} (Eqn 5):

$\Delta\Delta H_f^0$ (HNCO → ClNCO) = $\Delta\Delta H_f^0$ (H-NH_2 → Cl-NH_2) – [$\Delta\Delta H_f^0$ (HNH_2 → $ClNH_2$) - $\Delta\Delta H_f^0$ (HNO → ClNO)] x [(EN(NCO) - EN(NH_2)]/ [EN(NO) - EN(NH_2)]] = 16 - {[16 - (-11.4)] x [7.9 - 6.5] : [8.5 - 6.5]} = ~ -3 kcal mol^{-1} (5).

Hence, ΔH_f^0 (ClN=C=O) = ΔH_f^0 (HNCO) (-27) - 3 ≈ -30 kcal mol^{-1}. We do not insist on either value of -3 for $\Delta\Delta H^o_f$ in Eqn 5 or on the value of -30 kcal mol^{-1} for ΔH_f^0 ClNCO since the interrelationship EN/ΔH_f^0 is not so straightforward as to be given by Eqn 5 but still extremely high $\Delta\Delta H^o_f$ values for H → Cl replacement 35.5 kcal mol^{-1} (Eqn 2) and even more 53 kcal mol^{-1} (Eqn 1) seem doubtful if compared with data of Eqns 3 and 4. Consequently, the ΔH^o_f ClNCO = 8.5 kcal mol^{-1} gained from experiment in Ref. 4 also appears to be doubtful.

We suggest the following explanation for the very high experimental value for ClNCO molecule enthalpy of formation. Since the latter was obtained from an experimental bond dissociation energy ΔH_f^0(ClNCO) = ΔH_f^0(Cl) + ΔH_f^0(NCO) - D_0(Cl-NCO), the high ΔH_f^0 value can be explained by involvement of structure for $[NCO]^\bullet$ free radical which differs from expected $^\bullet$N=C=O structure, *e.g.* cyclic one cyclo-$NOC^\bullet$ (I) which obviously might have much higher ΔH_f^0 compared with linear $^\bullet$N=C=O isomer. Recently, the same group of authors observed formation of a cyclic isomer cyclo-$N_3^\bullet$ (II) in addition to azide free radical $^\bullet N_3$ in photofragmentation study of Cl-N_3 (azide) molecule [11]. The moieties -N=C=O and -N=N(+)=$N^\bullet$ are isoelectronic, so therefore our suggestion about involvement of cyclic $[NCO]^\bullet$ isomer seems reasonable.



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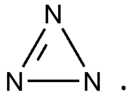
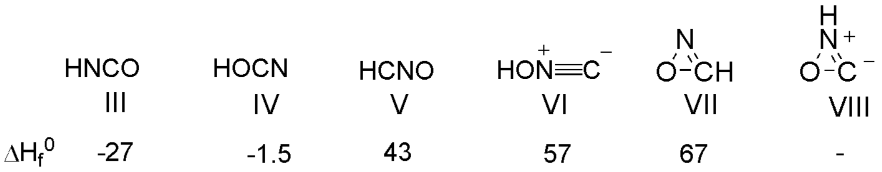


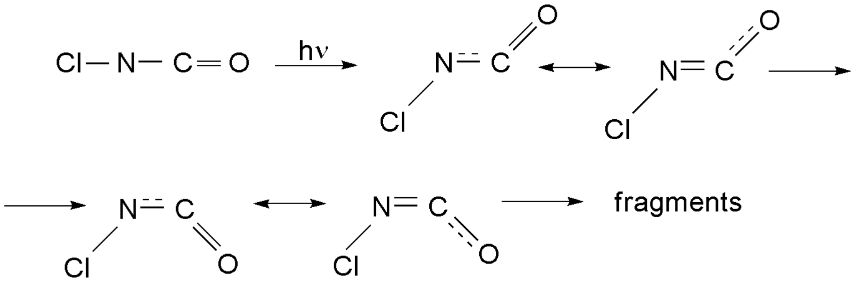
II

There is another possibility to be discussed to obtain the high D_0(Cl-NCO) value, this is isomerization of initial molecule in course of experiment. For [HCNO] species there are 6 possible isomers (ΔH_f^o - in kcal mol^{-1} - from Ref. 6)



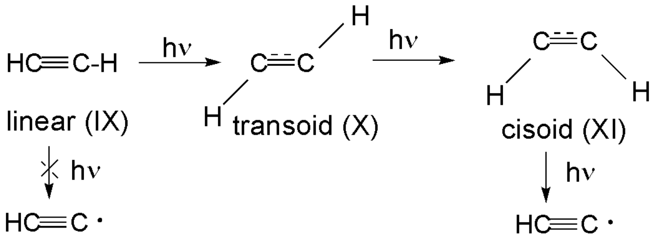
Thus we have to consider the enthalpies of formation for all isomers when H is replaced by Cl-atom. H → Cl replacement at C-atom exhibits rather small ΔH_f^0 values, e.g. $\Delta\Delta H_f^0$ ($CH_4 \rightarrow CH_3Cl$) ~ -1.8 or $\Delta\Delta H_f^0$ ($C_2H_4 \rightarrow ClC_2H_3$) 7.3 kcal mol^{-1} with ΔH_f^0values (ClC_2H_3) 5.2 kcal mol^{-1} [2]. Therefore, the ΔH_f^o values for isomers V or VII at H → Cl replacement will still give rather high ΔH_f^0 values for ClCNO or cyclo-NOCCl isomers, respectively, while we need to have low ΔH_f^0 [Cl, C, N, O] values to gain low D_0 values: D_0[Cl-(C,N,O)] = ΔH_f^0(Cl) + ΔH_f^0(NCO) - ΔH_f^0 [Cl, C, N, O] (isomers V and VII) (Eqn 6). Similarly, the H → Cl replacement in isomers IV, VI or XVIII will hardly lead to low ΔH_f^0 value for [Cl, C, N, O] molecules to gain high experimental D_0 values (Eqn 6). The authors [4] admit the possibility of formation of cyclic [ClNCO] isomer in course of reaction of linear ClNCO with photon but not link it with thermochemistry of the process.

There is the third possibility to obtain the higher ΔH_f^0 value for D_0 Cl-NCO value this is the "electronic isomerization" of initial ClNCO molecule (Eqn 6).



(6)

In such case, we obtain $[NCO]^{\bullet}$ (whatever its structure is) in an excited state. Such "electronic isomerization" was described in detail in case of photofragmentation of acetylene HC≡CH molecule (see Ref. 6).



(7)

With some photofragmentation methods $HC{\equiv}C^{\bullet}$ free radical is obtained from "isomer" X thus giving ΔH_f^0 of $HC{\equiv}C^{\bullet}$ 131[12] or 130.6 [13] kcal mol^{-1}, with other methods the further "isomerization" X → XI occurs leading to ΔH_f^0 $HC{\equiv}C^{\bullet}$ 136-140 kcal mol^{-1} (see Ref. 6).

Thus, in all known photofragmentation studies the $HC{\equiv}C^{\bullet}$ radical is obtained only in excited state and its enthalpy of formation in the ground state cannot be gained by this method. But its ΔH_f^0 can be obtained in chemical kinetic experiments, from IR spectra and some empirical estimations (see Ref. 6). Similarly, in our opinion, the enthalpy of formation of ClN=C=O and of other XNCO molecules could hardly be obtained in photofragmentation experiments.

We also perform computation of ΔH_f^0 for ClNCO molecule by semi-empirical methods applying isodesmic reaction [14] (Eqn 8)

Method	$HN{=}C{=}O$ +	$ClN{=}O$ →	$ClNC{=}O$ +	$HN{=}O - H_R$
ΔH_f^0 (kcal mol^{-1})	-27	12.4	[X]	23.8
MNDO/3			-30.3	8.1
MNDO			-32.6	5.8
AM1			-33.0	5.4
PM3			-35.9	2.5

(8)

Thus, all three methods give much lower values compared to that obtained in Ref. 4. We would prefer here the result gained by MINDO/3 method since namely by this method earlier the best results were obtained for $CH_2{=}C{=}O$ molecule (analogue of ClN=C=O) and other molecules of A=B=C series: -20.74 (MINDO/3), -6.83 (MNDO), -5.71(AM1), -9.27 (PM3) while the empirically found ΔH_f^0 ($CH_2{=}C{=}O$) was -23 – (-24) kcal mol^{-1} (from Ref. 1).

MINDO/3 for FN=C=O molecule does not give any deviation from other methods (compare with ketene $CH_2{=}C{=}O$ molecule): -59.3 (MNDO/3), -59.9 (MNDO), -57.3 (AM1) and -60.3 (PM3). Unfortunately, MINDO/3 could not be applied to BrNCO and INCO because there are no parameters for Br- and I-atoms at this method.

The drastic difference between our results and those found in the work of Ji et al [4] can be explained by application of diverse calculation schemes exercised in both works. While Ji et al involved calculation of atomization energies for HNCO and ClNCO molecules we used isodesmic reaction (Eqn 8) with the species closely related structurally to the target ClNCO molecule. The latter procedure usually gives better results.

Now we represent the literature data on the enthalpies of formation ΔH_f^0 and enthalpic shifts $\Delta\Delta H_f^0$ (at arrows) for two series of compounds XNH_2 (from Ref. 9) and XNO [10] (Eqns 9 and 10) [ΔH_f^0 and $\Delta\Delta H_f^0$ – in kcal mol^{-1}):

$$\begin{array}{lccccccc} & FNH_2 & \xrightarrow{+16.5} & ClNH_2 & \xrightarrow{+15} & BrNH_2 & \xrightarrow{+13} & INH_2 \\ \Delta H_f^0 & -11.5 & & 5 & & 20 & & 33 \end{array} \qquad (9)$$

$$\begin{array}{lccccccc} & FNO & \xrightarrow{+28.1} & ClNO & \xrightarrow{+7.2} & BrNO & \xrightarrow{+9.4} & INO \\ \Delta H_f^0 & -15.7 & & 12.4 & & 19.6 & & 29 \end{array} \qquad (10)$$

Similarly, we give our computation results on $\Delta\Delta H_f^0$ values for the XN=C=O series [ΔH_f^0 and

$\Delta\Delta H_f^0$ (at arrows) – in kcal mol^{-1}] (Eqns 11 and 12)

$$\begin{array}{llllll} & & FN{=}C{=}O \xrightarrow{+14.5} & Cl{=}C{=}O \xrightarrow{+1.2} & BrN{=}C{=}O \xrightarrow{-10.2} & IN{=}C{=}O \\ \text{MNDO} & \Delta H_f^0 & -38.7 & -14.2 & -13.0 & -23.2 \end{array} \qquad (11)$$

$$\begin{array}{llllll} & & FN{=}C{=}O \xrightarrow{+12.2} & Cl{=}C{=}O \xrightarrow{-3.0} & BrN{=}C{=}O \xrightarrow{-1.1} & IN{=}C{=}O \\ \text{AM1} & \Delta H_f^0 & -27.9 & -15.7 & -18.7 & -19.8 \end{array} \qquad (12)$$

From EN values for NH_2- (6.5), -N=C=O (7.9) and -N=O (8.5) groups (see above) the enthalpic shifts, the $\Delta\Delta H_f^0$ for XNCO series at F → Cl → Br → I replacement should be *intermediate* between those for XNH_2 and XN=O series. However we see that all the $\Delta\Delta H_f^o$ values in Eqns 11 and 12 are appeared to be very far from the expected ones. Moreover, there are 3 negative (?) and one small positive $\Delta\Delta H_f^o$ values (+1.2 kcal mol^{-1}) which are inconsistent with the tendencies at F → Cl → Br → I substitution in XNH_2 and XNCO series. Hence, we can conclude that both semi-empirical methods, MNDO and AM1, failed in computation of ΔH_f^o XNCO species.

Now we analyze the data of PM3 computation scheme repeating - for comparison - the experimental data on XNH_2 and XNO and our empirical results for XNCO series [ΔH_f^o and $\Delta\Delta H_f^o$ (at arrows) in kcal mol^{-1} (Eqns 9, 10, 13 and 14)

$$\begin{array}{lllll} & FNH_2 \xrightarrow{+16.5} & ClNH_2 \xrightarrow{+15} & BrNH_2 \xrightarrow{+13} & INH_2 \\ \Delta H_f^0 & -11.5 & 5 & 20 & 33 \end{array} \qquad (9)$$

$$\begin{array}{lllll} & FNCO \xrightarrow{+24.4} & ClNCO \xrightarrow{+7.7} & BrNCO \xrightarrow{+9.5} & INCO \\ \Delta H_f^0(\text{PM3}): & -60.3 & -35.9 & -28.2 & -18.70 \end{array} \qquad (13)$$

$$\begin{array}{lllll} & FNCO \xrightarrow{+25} & ClNCO \xrightarrow{+9.5} & BrNCO \xrightarrow{+10.3} & INCO \\ \Delta H_f^{0}{*}: & -55 & -30 & -20.5 & -10.2 \end{array}$$

* from empirical calculations (see above) (14)

$$\begin{array}{lllll} & FNO \xrightarrow{+28.1} & ClNO \xrightarrow{+7.2} & BrNO \xrightarrow{+9.4} & INO \\ \Delta H_f^0 & -15.7 & 12.4 & 19.6 & 29 \end{array} \qquad (10)$$

We see that PM3 results for ClNCO and BrNCO molecules are rather close to our empirical results both in ΔH_f^o and $\Delta\Delta H_f^o$ (ClNCO → BrNCO) values thus supporting our empirical procedure. In addition, the $\Delta\Delta H_f^o$ at Cl → Br replacement appears to be intermediate for such replacement in XNH_2 and XNO series. However, the computed ΔH_f^o values for FNCO and INCO molecules lead to $\Delta\Delta H_f^o$ for F → and Br → I substitution which are very far from the tendencies following from both experimental (for XNH_2 and XNO series) and empirical ones for XNCO molecules. We report that the $\Delta\Delta H_f^o$ for the latter should be intermediate between those for XNH_2 and XNO series. Thus, rounding up the values for INCO molecule (-10.2 to -10 kcal mol^{-1}) we represent our final results on the enthalpies of formation for XN=C=O molecules: -55 (F), -30 (Cl), -20.5 (Br) and -10 kcal mol^{-1} (I). Probably for FNCO molecule its ΔH_f^o value might be slightly more positive -52 - (-53) kcal mol^{-1} to fit the tendencies in $\Delta\Delta H_f^o$ ($FNH_2 \rightarrow ClCH_2$) and ($FNO \rightarrow ClNO$) replacement.

We think that in the absence of experimental thermochemical data for XN=C=O molecules or their controversial value (see above) our data, although being approximate ones, could be used in practice.

Now we can proceed to the estimation of the enthalpies of formation of other A=B=C and A=B=C=D type species. Applying the enthalpic shift for ΔH_f^o HN=C=O $\rightarrow$ ΔH_f^o HN=C=S = -27[2] $\rightarrow$ 30 [10] = 57 kcal mol^{-1} we can now estimate the enthalpies of formation for other XN=C=S molecules (for ΔH_f^o of XN=C=O see above)

$\Delta H_f^0[ClN{=}C{=}S] = \Delta H_f^0[ClN{=}C{=}O] + \Delta\Delta H_f^0(HN{=}C{=}O \rightarrow HN{=}C{=}S) = -30 + 57 = 27$ kcal mol^{-1}
$\Delta H_f^0[BrN{=}C{=}S] = \Delta H_f^0[BrN{=}C{=}O](-20.5) + 57 = 36.5$ kcal mol^{-1}
$\Delta H_f^0[IN{=}C{=}S] = \Delta H_f^0[IN{=}C{=}O](-10) + 57 = 47$ kcal mol^{-1}

However, for FN=C=S molecule we introduce the small arbitrary correction term. We think that in FN=C=O molecule there exists certain F/CO (two strong acceptors) repulsion which is absent in FN=C=S molecule. Hence,
$\Delta H_f^0[FN{=}C{=}S] = \Delta H_f^0[FN{=}C{=}O](-53) + 57 + \Delta(\sim - 2) = \sim 2$ kcal mol^{-1}

Similarly, using the enthalpies of formation for $CH_2{=}C{=}S$ (38) and $CH_2{=}C{=}Se$ (60 kcal mol^{-1}) [7] and, consequently, the enthalpic shift $\Delta\Delta H_f^0$ ($CH_2{=}C{=}S \rightarrow CH_2{=}C{=}Se$) = 60 - 38 =22 kcal mol^{-1} we gain ΔH_f^0 [HN=C=Se] = ΔH_f^0 [HN=C=S] (30) + 22 = 52 kcal mol^{-1}. Now we can estimate ΔH_f^0 of XN=C=Se molecules adding 22 kcal mol^{-1} to ΔH_f^0 XN=C=S. Thus, we obtain ΔH_f^0 XN=C=Se: 24 (F), 49 (Cl), 58.5 (Br) and 69 kcal mol^{-1} (I).

As an example, we can estimate the enthalpy of formation for compound XVIII, e.g. $CH_2{=}C{=}C{=}C{=}S$ molecule: ΔH_f^0 (XVIII) = ΔH_f^0 ($CH_2{=}C{=}S$) + 2 C_a (where C_a is the Benson group contribution for cumulenic carbon C=C=C) = 38 [7]+ 2 (34.6) [7] = 107.2 ~ 107 kcal mol^{-1}.

An interesting cumulene type system is the dimer of carbon monoxide O=C=C=O which has not been yet synthesized despite many attempts to do it. The question arises whether this molecule is thermodynamically stable. We present now the empirical calculation of its enthalpy of formation: ΔH_f^o [O=C=C=O] = 2 ΔH_f^o [$CH_2{=}C{=}O$] - ΔH_f^o [$CH_2{=}CH_2$] + Δ = 2 (-24) [6] - 12.5 [2] + Δ (Eqn 15) = -60.5 + Δ kcal mol^{-1} while the sum of ΔH_f^0 of decomposition products, i.e. for two ΔH_f^0 (CO) is 2x(-26.2) = -52.4 kcal mol^{-1}. Thus at the beginning, it seems that O=C=C=O molecule is thermodynamically stable if the Δ correction term is < ~8 kcal mol^{-1}. This correction term might appear due to expected repulsion of two powerful electron withdrawing CO/CO groups destabilizing the system. Now we try to estimate this correction term.

Leaning on close EN values for CHO- (7.2) and CHF_2-groups (7.3) [6], we adjust the repulsive interaction of two CO-groups in O=C=C=O to that existing in $CF_2=CF_2$ molecule. We think that steric cis- F/F interaction is of minor importance due to small size of F-atoms. So, ΔH_f^0 (calc)[$CF_2=CF_2$] = 2 ΔH_f^0 [$CF_2=CH_2$] - ΔH_f^0 [$CH_2=CH_2$] = 2 (-80.1) [2] - 12.5 [2] = -172.7 while ΔH_f^0 (exp)[$CF_2=CF_2$] is -157.5 [2] kcal mol^{-1} (Eqn 16). Thus destabilization of the molecule due to repulsive CF_2/CF_2 interaction exhibits -157.5 - (-172.7) = 15.2 kcal mol^{-1}. Hence, ΔH_f^0 (calc)[O=C=C=O] = 2 ΔH_f^0 [CH_2=C=O] - ΔH_f^0 [$CH_2=CH_2$] + Δ = 2 (-24) [7] - 12.5 [2] + 15.2 = -45.3 kcal mol^{-1} (Eqn 17); while the sum of ΔH_f^o of its decomposition products two CO molecules is 2 (-26.2) = -52.4[10] kcal mol^{-1}. The reality of CO/CO strong interaction is supported by calculated ΔH_f^0 deviation from additivity in its analogue C_3O_2 molecule. ΔH_f^0 [O=C=C=C=O](calc) = 2 ΔH_f^0 [CH_2=C=O] + ΔH_f^0 [$CH_2=C=CH_2$] – 2 ΔH_f^0 [$CH_2=CH_2$] = 2 (-24) + 45.5 – 2 (12.5) = -27.5 kcal mol^{-1} (Eqn 18) whereas ΔH_f^0 (exp) = -23.4 [2] kcal mol^{-1} leading to destabilization of –23.4 – (-27.5) = 4.1 kcal mol^{-1}.

We think, that rather strong CO/CO repulsive interaction in β-position in O=C=C=C=O molecule stands in line with expected larger CO/CO interaction in α-position in O=C=C=O molecule 15.2 kcal mol^{-1} (see above). So, comparing the ΔH_f^0 (calc) for the latter, -45.3 with the $\Sigma\Delta H_f^0$ [2 CO](-52.4 kcal mol^{-1}) we see that if the barrier for reaction O=C=C=O → 2 CO is a small one than the dimer of carbon monoxide is thermodynamically unstable molecule and cannot be synthesized. However, if such barrier is > ~8 kcal mol^{-1} [-45.3 – (-52.4)] its synthesis becomes quite realistic. We notice, that structurally close O=C(•)-O-Me free radical is stable *kinetically* while being unstable *thermodynamically*, compare its ΔH_f^0 -40.4[7] with Σ [CO_2 + Me] = -94.1 [5] + 55.1 [7] = -59.0 kcal mol^{-1}. Up to now all attempts to observe O=C=C=O molecule in mass spectrometer applying collision activation (CA) techniques have failed [15]. However, as it is thoroughly examined in Ref. 7 at the CA process the collision gas (usually, He) can play an active role as the "catalyst" decreasing the energetical barrier, in our case, for reaction O=C=C=O → 2 CO. Thus, other ways of O=C=C=O synthesis might be exercised where any forms of catalysis are excluded.

For calculation of ΔH_f^o for S=C=C=S we apply the same scheme as for O=C=C=O molecule (see above): ΔH_f^o [S=C=C=S] = 2 ΔH_f^o [CH_2=C=S] - ΔH_f^o [$CH_2=CH_2$] + Δ = 2 (38) [6] - 12.5 [2] + Δ = 63.5 kcal mol^{-1} + Δ (Eqn 19)

We expect destabilization for CS/CS interaction being essentially weaker compared with CO/CO interaction in O=C=C=O molecule. But we cannot use $Cl_2C=CCl_2$ molecule as a model for calculation of such destabilization in S=C=C=S molecule since, firstly, EN of $CHCl_2$ and CHS differ essentially 6.2 and 6.8 units, respectively [6], and secondly, both steric and polar Cl/Cl interaction do exist in $Cl_2C=CCl_2$ molecule when compared with two $Cl_2C=CH_2$ molecules. Our calculation of summary destabilization of Cl/Cl interaction is 8.7 kcal mol^{-1}. Thus, from Δ in Eqn 19 we take an arbitrary value of, say, ~4.5 kcal mol^{-1} and obtain ΔH_f^0 (S=C=C=S) ~ 68 kcal mol^{-1} while the sum of ΔH_f^0 of its decomposition products two CS is 2 (64) [7] = 128 kcal mol^{-1}. So, S=C=C=S thermodynamically is a stable species. Ab initio computation of ΔH_f^o of the latter from ΔH_R = 33.7 kcal mol^{-1} for S=C=C=S → 2 CS gives the very high value 95.3 [16] if the ΔH_f^0 for CS 64 kcal mol^{-1} is used.
Finally, ΔH_f^0 (calc.)[Se=C=C=Se] = 2 ΔH_f^0 [CH_2=C=Se] - ΔH_f^0 [$CH_2=CH_2$] = 2 (60) [6] - 12.5 [2] + Δ = 107.5 + Δ. Applying an arbitrary minor value 0.5 for Δ we get ΔH_f^0 [Se=C=C=Se] ~ 108 kcal mol^{-1}.

CONCLUSIONS

Applying combination of empirical and semi-empirical methods the enthalpies of formation for 15 heterocumulenes of the types A=B=C and A=B=C=O were estimated. Empirical procedures were based on enthalpic shifts and the new electronegativity scale. Most of semi-empirical results appeared to be unsatisfactory and could be treated only together with empirically gained values. The possibilities of synthesis of carbon monoxide dimer O=C=C=O are discused. Its enthalpy of formation is estimated as -45.5 kcal mol^{-1} which only by ~7 kcal mol^{-1} is higher than that of its fragments – two CO molecules.

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