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APPLICATION OF THE SETH-PAUL-VAN DUYSE EQUATION – II[1]

TRANSMISSION OF POLAR EFFECTS BY THE CH=CH GROUP

A. PERJÉSSY*
Department of Organic Chemistry, Komensky University, 80100 Bratislava, Czechoslovskia

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Abstract – The use of the improved Seth-Paul-Van Duyse equation (SPVDE) provides a new statistically significant method for determination of transmissive factors of polar effects for various bridge groups. The method was applied to the C=O stretching frequencies of s-*cis* and s-*trans* conformers of 98 $R_1CH=CHCOR_2$ compounds. The transmissive factors for CH=CH group in both conformations s-*cis* and s-*trans* have been calculated with an accuracy about of one order higher than found by using the methods described earlier. The applicability of the improved SPVDE to the 137 C=O stretching frequencies of various $R_1CH=CHCOR_2$ compounds has been proved.

In preceding paper[1] we reinvestigated the original SPVDE[2] and derived a simple relation defining new $X^+(R)$ substituent constants on the basis of electrophilic σ^+ constants. It was shown that these substituent constants fit very well the improved SPVDE and allow the extension of its validity for a wide range of carbonyl compounds.

A number of papers[3-16] have been devoted to the quantitative study of the transmission of polar effects by the CH=CH group using linear free-energy relationships (LFER) between the various physicochemical properties and various substituent constants. The number of compounds used in the individual series investigated varied from 5 to 14. The slopes of the such LFERs was determined[17] in most cases with an accuracy of ± 15%. The values of the transmissive factors (π') for the CH=CH group reported earlier[3-16] were found to be in the region of 0·42–0·96 when using various physicochemical properties in LFERs. However, when using the same physicochemical property (i.e. C=O stretching frequency) in LFERs the range of transmissive factors[3-9] ($\pi' = 0{\cdot}58–0{\cdot}91$) did not differ significantly from the range mentioned above. A statistical analysis[18] of the literature data[3-9] shows that the transmissive factors for CH=CH group can be determined with an accuracy from 9% to 33%. Considering this relatively low accuracy of determination of π' it is difficult in some cases to distinguish quantitatively the transmissive ability of two similar bridge groups.

The aim of this work was therefore to develop a new, more reliable, method for determination of transmissive factors of polar effects. For this purpose we investigated statistically significant correlations between the C=O stretching frequencies of a relatively large number of $R_1CH=CHCOR_2$ compounds and $X^+(R)$ constants[1,2] and compared them with the improved SPVDE[1] obeyed by the carbonyl stretching frequencies of 439 R_1COR_2 compounds.

The C=O stretching frequencies of s-*cis* and s-*trans* conformers of $R_1CH=CHCOR_2$ compounds (measured in dilute CCl_4) together with the corresponding $\Sigma X^+(R')$ values are listed in Table 1. The $\Sigma X^+(R')$ values are defined in the scale of $X^+(R)$ constants[1,2] fitting the SPVDE, but neglecting the CH=CH bridge group:

$$\sum X^+(R') = X^+(R_1) + X^+(R_2). \qquad (1)$$

As the $X^+(R)$ constant of the $N(Me)_2$ group is lacking in the papers[1,2], we determined it (Table 2) using the carbonyl stretching frequencies of a series of fourteen substituted N,N-dimethylbenzamides[24]: $X^+(R) = 0{\cdot}562$. Correlating the carbonyl stretching frequencies of s-*cis* and s-*trans* conformers of $R_1CH=CHCOR_2$ compounds (series I and II respectively) with corresponding $\Sigma X^+(R')$ values (Table 1) we obtained two statistically significant relationships:

$$\nu(CO)_{s\text{-}cis} = 29{\cdot}276 \sum X^+(R') + 1611{\cdot}385 \qquad (2)$$

and

$$\nu(CO)_{s\text{-}trans} = 32{\cdot}672 \sum X^+(R') + 1582{\cdot}431. \qquad (3)$$

The result is shown in Fig 1 and the statistical treatment of correlations is listed in Table 3. Applying the improved SPVDE[1] (valid for R_1COR_2 compounds, series III):

$$\nu(CO) = 38{\cdot}219 \sum X^+(R) + 1583{\cdot}426 \qquad (4)$$

we can calculate the transmissive factors for CH=CH group in both s-*cis* and s-*trans* con-

Table 1. Carbonyl stretching frequencies and $\Sigma X^{+}(R')$ and $\Sigma X^{+}(R)$ values of $R_1CH{=}CHCOR_2$ compounds

			$\nu(CO)^b$				$\sum X^{+}(R)$	
Compound	R_1^a	R_2^a	s-*trans*	s-*cis*	Ref	$\sum X^{+}(R')$	s-*trans*	s-*cis*
1	4-N(Me)$_2$Ph	H	1677·0		4	2·802	2·370	
2	4-OMePh	H	1685·0		4	3·021	2·557	
3	4-MePh	H	1687·0		4	3·133	2·653	
4	Ph	H	1688·0		4	3·200	2·710	
5	4-ClPh	H	1689·5		4	3·233	2·738	
6	3-ClPh	H	1691·0		4	3·302	2·797	
7	3-BrPh	H	1691·0		4	3·302	2·797	
8	3-NO$_2$Ph	H	1693·5		4	3·366	2·852	
9	4-NO$_2$Ph	H	1694·0		4	3·395	2·877	
10	4-N(Me)$_2$Ph	Ph	1642·0	1663·0	9	1·742	1·463	2·065
11	4-NH$_2$Ph	Ph	1645·0	1667·0	9	1·838	1·545	2·139
12	4-OMePh	Ph	1648·0	1670·0	9	1·961	1·651	2·233
13	4-MePh	Ph	1652·0	1672·0	9	2·073	1·746	2·319
14	4-PhPh	Ph	1648·0	1670·0	9	2·107	1·775	2·345
15	Ph	Ph	1653·0	1672·0	9	2·140	1·804	2·370
16	4-FPh	Ph	1655·0	1675·0	9	2·148	1·811	2·376
17	4-ClPh	Ph	1655·0	1675·0	9	2·173	1·832	2·396
18	3-ClPh	Ph	1657·0	1676·0	9	2·242	1·891	2·448
19	4-CNPh	Ph	1658·0	1676·0	9	2·304	1·944	2·496
20	3-NO$_2$Ph	Ph	1660·0	1678·0	9	2·306	1·946	2·497
21	4-N(Me)$_2$Ph	Me	1666·0	1688·9	19	2·479	2·094	2·630
22	4-OMePh	Me	1670·0	1693·0	20	2·698	2·281	2·798
23	4-PhPh	Me	1674·0	1696·9	19	2·844	2·406	2·910
24	Ph	Me	1676·4	1697·7	21	2·877	2·434	2·935
25	4-ClPh	Me	1677·2	1699·2	19	2·910	2·462	2·960
26	4-BrPh	Me	1678·3	1699·3	19	2·920	2·471	2·968
27	4-CNPh	Me	1680·0	1701·1	19	3·041	2·574	3·060
28	4-NO$_2$Ph	Me	1680·8	1702·0	19	3·072	2·601	3·084
29	Ph	Et	1674·6	1697·2	21	2·828	2·392	2·897
30	4-OMePh	Et	1670·0	1695·0	20	2·649	2·239	2·760
31	Ph	nPr	1672·5	1695·4	21	2·828	2·392	2·897
32	Ph	nBu	1675·0	1695·0	22	2·820	2·385	2·891
33	2-ClPh	nBu	1679·0	1698·0	22	2·985	2·526	3·018
34	3-ClPh	nBu	1681·0	1698·0	22	2·922	2·472	2·969
35	4-ClPh	nBu	1679·0	1697·0	22	2·853	2·413	2·916
36	2,4-Cl$_2$Ph	nBu	1681·0	1701·0	22	3·018	2·554	3·043
37	3,4-Cl$_2$Ph	nBu	1681·0	1698·0	22	2·955	2·501	2·995
38	2,6-Cl$_2$Ph	nBu	1681·0	1702·0	22	3·150	2·667	3·144
39	4-MePh	nBu	1670·0	1692·0	22	2·753	2·328	2·840
40	4-OMePh	nBu	1666·0	1690·0	22	2·641	2·232	2·754
41	3,4-(OMe)$_2$Ph	nBu	1664·0	1692·0	22	2·660	2·248	2·769
42	4-N(Me)$_2$Ph	nBu	1659·0	1683·0	22	2·422	2·045	2·586
43	2-FPh	nBu	1677·0	1695·0	22	2·863	2·422	2·924
44	Ph	nPe	1673·0	1694·0	22	2·820	2·385	2·891
45	Ph	iPr	1671·0	1694·0	20	2·778	2·349	2·859
46	Ph	iBu	1669·3	1693·7	21	2·804	2·371	2·879
47	Ph	2-Thi	1636·0	1661·0	1	1·752	1·472	2·073
48	Ph	2-Fu	1642·0	1669·0	1	1·923	1·618	2·204
49	Ph	tBu		1687·0	20	2·728		2·821
50	4-N(Me)$_2$Ph	OH		1724·0	3	3·772		3·620
51	4-OMePh	OH		1728·0	3	3·991		3·788
52	4-MePh	OH		1730·0	3	4·103		3·874
53	Ph	OH		1733·0	3	4·170		3·925
54	3-OMePh	OH		1732·0	3	4·189		3·940
55	4-ClPh	OH		1731·0	3	4·203		3·950
56	3-ClPh	OH		1735·0	3	4·272		4·003
57	3-BrPh	OH		1735·0	3	4·272		4·003
58	3-NO$_2$Ph	OH		1742·0	3	4·336		4·062
59	4-NO$_2$Ph	OH		1740·0	3	4·365		4·075
60	Ph	OMe		1727·0	23	3·840		3·672
61	2-ClPh	OMe		1727·0	23	4·005		3·799

Table 1—*Continued*

Compound	R_1^a	R_2^a	$\nu(CO)^b$ s-*cis*	Ref	$\Sigma X^+(R')$	$\Sigma X^+(R)$ s-*cis*
62	2-BrPh	OMe	1727·0	23	4·090	3·864
63	2-OMePh	OMe	1726·0	23	3·650	3·527
64	2-NO_2Ph	OMe	1731·0	23	4·240	3·979
65	4-OMePh	OEt	1713·5	5	3·461	3·382
66	4-MePh	OEt	1716·0	5	3·573	3·468
67	Ph	OEt	1717·0	5	3·640	3·519
68	4-ClPh	OEt	1717·0	5	3·673	3·545
69	3-NO_2Ph	OEt	1721·0	5	3·806	3·646
70	4-NO_2Ph	OEt	1722·0	5	3·835	3·669
71	4-NO_2Ph	$N(Me)_2$	1660·9	24	1·827	2·130
72	4-CNPh	$N(Me)_2$	1660·4	24	1·796	2·107
73	4-BrPh	N(Me)	1658·8	24	1·675	2·014
74	4-ClPh	$N(Me)_2$	1658·5	24	1·665	2·006
75	4-FPh	$N(Me)_2$	1659·6	24	1·662	2·004
76	Ph	$N(Me)_2$	1658·1	24	1·632	1·981
77	4-MePh	$N(Me)_2$	1657·0	24	1·565	1·930
78	4-OMePh	$N(Me)_2$	1656·2	24	1·453	1·844
79	3-NO_2Ph	$N(Me)_2$	1661·8	24	1·798	2·108
80	3-CNPh	$N(Me)_2$	1661·9	24	1·772	2·088
81	3-BrPh	$N(Me)_2$	1659·8	24	1·734	2·059
82	3-ClPh	$N(Me)_2$	1660·1	24	1·734	2·059
83	3-FPh	$N(Me)_2$	1659·9	24	1·722	2·050
84	3-MePh	$N(Me)_2$	1657·7	24	1·622	1·973
85	3-OMePh	$N(Me)_2$	1658·1	24	1·651	1·996
86	Ph	Fer	1660·0	25	1·778	2·093
87	4-$N(Me)_2$Ph	Fer	1656·0	25	1·380	1·788
88	4-NH_2Ph	Fer	1657·5	25	1·476	1·862
89	4-OMePh	Fer	1658·0	25	1·599	1·956
90	4-MePh	Fer	1658·5	25	1·711	2·042
91	4-FPh	Fer	1660·5	25	1·768	2·085
92	4-ClPh	Fer	1661·0	25	1·811	2·118
93	3-ClPh	Fer	1662·0	25	1·880	2·171
94	3-NO_2Ph	Fer	1665·5	25	1·944	2·220
95	4-NO_2Ph	2-Fu	1673·0	26	2·118	2·353
96	2-Thi	2-Thi	1665·0	27	1·364	1·776
97	2-Fu	2-Fu	1667·0	27	1·706	2·038
98	Fer	Fer	1658·0	18	1·416	1·816

[a] Abbreviations: Thi—thienyl, Fu—furyl, Fer—ferrocenyl.
[b] Measured in CCl_4 and given in cm^{-1}.

formations as follows:

$$\pi'(CH{=}CH)_{s\text{-}cis} = \rho_I/\rho_{III} = 0{\cdot}766 \pm 0{\cdot}012 \quad (5)$$

and

$$\pi'(CH{=}CH)_{s\text{-}trans} = \rho_{II}/\rho_{III} = 0{\cdot}855 \pm 0{\cdot}024 \quad (6)$$

where ρ_I, ρ_{II} and ρ_{III} are the slopes of the corresponding linear correlations in series I, II and III.

As it follows from Eqs 5 and 6, the transmissive factors for CH=CH group in s-*cis* and s-*trans* conformations were determined with an accuracy of 1·6 and 2·8% respectively. The value of the transmissive factor determined experimentally for the CH=CH group in s-*cis* conformation is in a satisfactory agreement with the theoretical value calculated[12] by Jaffe (0·683) using an MO method. From the above results it can be concluded that the application of the improved SPVDE provides a new statistically significant method for determination of transmissive factors, the accuracy of which is of about one order higher than the methods described earlier.[3-16] It can be also confirmed that the transmissive ability of the CH=CH group in the s-*cis* conformation is somewhat lower than that in the s-*trans* conformation. This may be probably caused by different coplanarity of two conformers as well as by the field effect which operate between the CH=CH and C=O groups.[20] A similar result was found in the case of *cis* and *gauche* conformers of monochloroacetates.[28] The following ratio was calculated between the transmissive factors for s-*cis* and s-*trans* conformers and between the corresponding slopes of ν(CO) *vs* ΣX(R′) correlations:

$$\pi'(CH{=}CH)_{s\text{-}cis}/\pi'(CH{=}CH)_{s\text{-}trans} = \rho_I/\rho_{II} = 0{\cdot}896$$

Table 2. Determination of $X^+(R)$ constant of the $N(Me)_2$ group from the carbonyl stretching frequencies of R_1COR_2 compounds (R_2=$N(Me)_2$)

R_1	$\nu(CO)^a$	$\sum X^+(R)^b$	$\sum X^+(R_2)^c$
4-NO_2Ph	1651·9	1·768	0·503
4-CNPh	1652·5	1·807	0·573
4-BrPh	1646·1	1·640	0·527
4-ClPh	1647·3	1·671	0·568
4-FPh	1646·8	1·658	0·598
Ph	1645·9	1·635	0·565
4-MePh	1644·1	1·588	0·585
4-OMePh	1642·5	1·546	0·655
3-NO_2Ph	1652·1	1·797	0·561
3-CNPh	1651·5	1·781	0·571
3-BrPh	1648·5	1·703	0·531
3-ClPh	1648·5	1·703	0·531
3-FPh	1648·2	1·695	0·535
3-MePh	1654·3	1·619	0·559
3-OMePh	1646·5	1·650	0·561
		Mean value:	0·562

[a] Carbonyl stretching frequencies (in cm^{-1}) measured in CCl_4 taken from Ref 24.

[b] Calculated using Eq 4.

[c] Calculated as follows: $X^+(R_2) = \Sigma X^-(R) - X^+(R_1)$.

Comparing Eq 4 with Eqs 2 and 3 respectively, it is possible to calculate the original $\Sigma X^+(R)$ values of s-*cis* and s-*trans* conformers of R_1CH=$CHCOR_2$ compounds according to the relation:

$$\sum X^+(R) = \pi'(CH{=}CH) \sum X^+(R') + z \quad (7)$$

where $\pi'(CH{=}CH)$ is 0·766 and 0·855 and z is 0·731 and −0·026 for the s-*cis* and s-*trans* conformers respectively. The $\Sigma X^+(R)$ values calculated for all 137 s-*cis* and s-*trans* conformers of R_1CH=$CHCOR_2$ compounds are listed in Table 1. The correlation of corresponding C=O stretching frequencies with $\Sigma X^+(R)$ values (series IV) is shown in Fig 2. The comparison of data in Table 3 shows that the regression parameters of this correlation practically do not differ from those of the improved SPVDE.[1] Thus, it can be concluded that the CO stretching frequencies of both s-*cis* and s-*trans* conformers of R_1CH=$CHCOR_2$ compounds fit the improved SPVDE well.

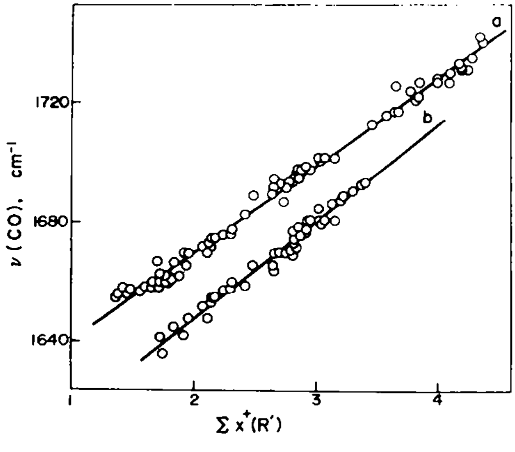

Fig 1. Plot of the C=O stretching frequencies *vs* $\Sigma X^+(R')$ values for R_1CH=$CHCOR_2$ compounds:
a – s-*cis* conformers
b – s-*trans* conformers.

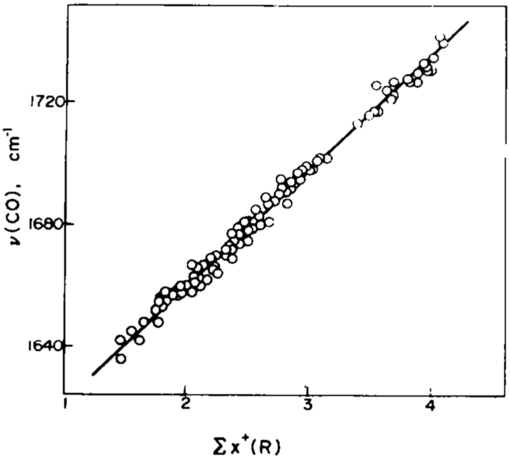

Fig 2. Plot of the C=O stretching frequencies *vs* $\Sigma X^+(R)$ values for R_1CH=$CHCOR_2$ compounds.

Table 3. Statistical treatment of linear correlations

Series	Compounds	Conformation	Correlation	n[a]	r[b]	ρ[c]	q[d]	s_ρ[e]	s_q[f]	s[g]
I	$R_1CH{=}CHCOR_2$	s-*cis*	ν(CO) *vs* $\Sigma X^+(R')$	89	0·995	29·276	1611·358	0·302	7·485	2·558
II	$R_1CH{=}CHCOR_2$	s-*trans*	ν(CO) *vs* $\Sigma X^+(R')$	48	0·988	32·672	1582·431	0·759	14·093	2·334
III	R_1COR_2	—	ν(CO) *vs* $\Sigma X^+(R)$	439	0·995	38·219	1583·426	0·185	12·694	2·998
IV	$R_1CH{=}CHCOR_2$	s-*cis* and s-*trans*	ν(CO) *vs* $\Sigma X^+(R)$	137	0·995	38·221	1583·411	0·329	9·938	2·463

[a] Number of points used in correlation.
[b] Correlation coefficient.
[c] Slope.
[d] Intercept.
[e] Standard deviation of ρ.
[f] Standard deviation of q.
[g] Standard deviation.

Note added in proof. It was found during the preparation of this paper that also some articles[29-32] published recently by Yanovskaya *et al.* have been devoted to the quantitative study of the transmission of polar effects by the CH=CH group. The number of compounds used in LFERs in these investigations varied from 4 to 9 and the transmissive factors for CH=CH group were found to be in the region of 0·51 to 0·90.

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