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Supplementary Information

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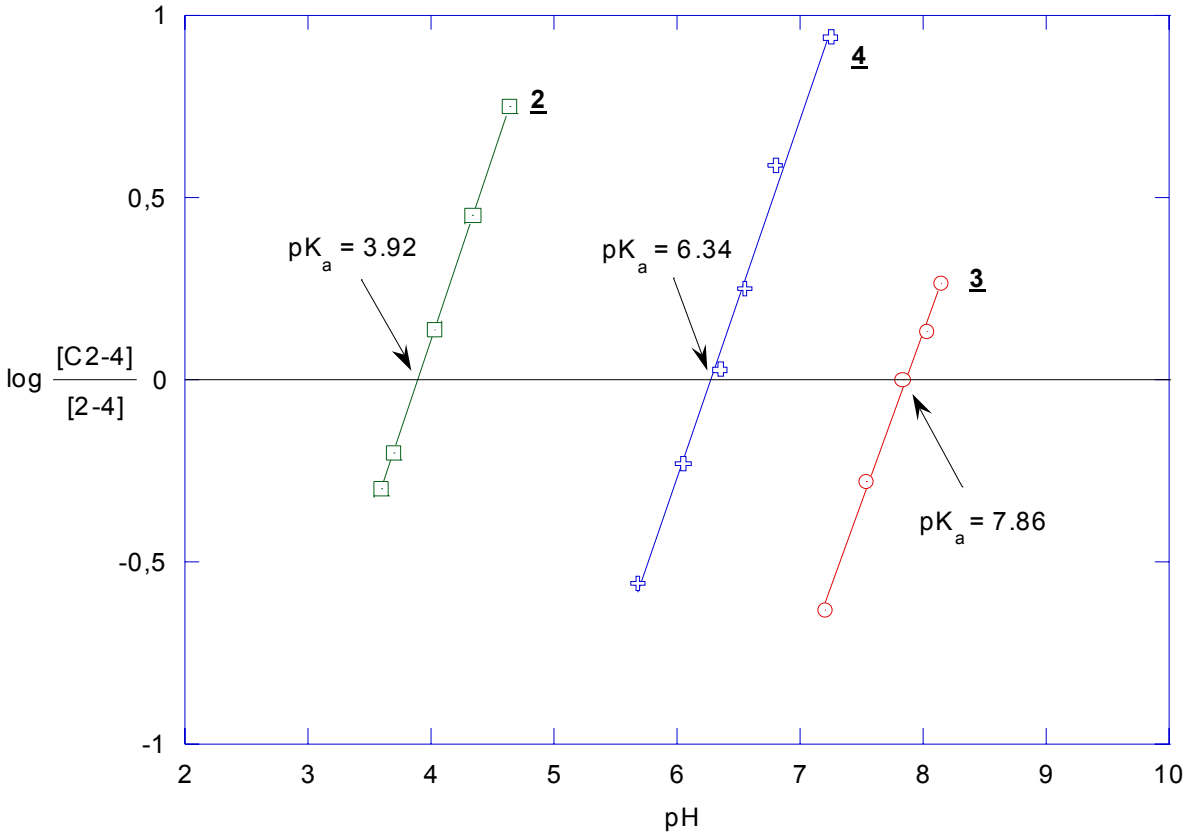

Figure S1 : Effect of pH on the σ-complexation of DNBZ (**2**), DNBS (**3**) and DNBSe (**4**) at T = 25 °C in aqueous solution; I = 0.2 mol dm^{-3} KCl.

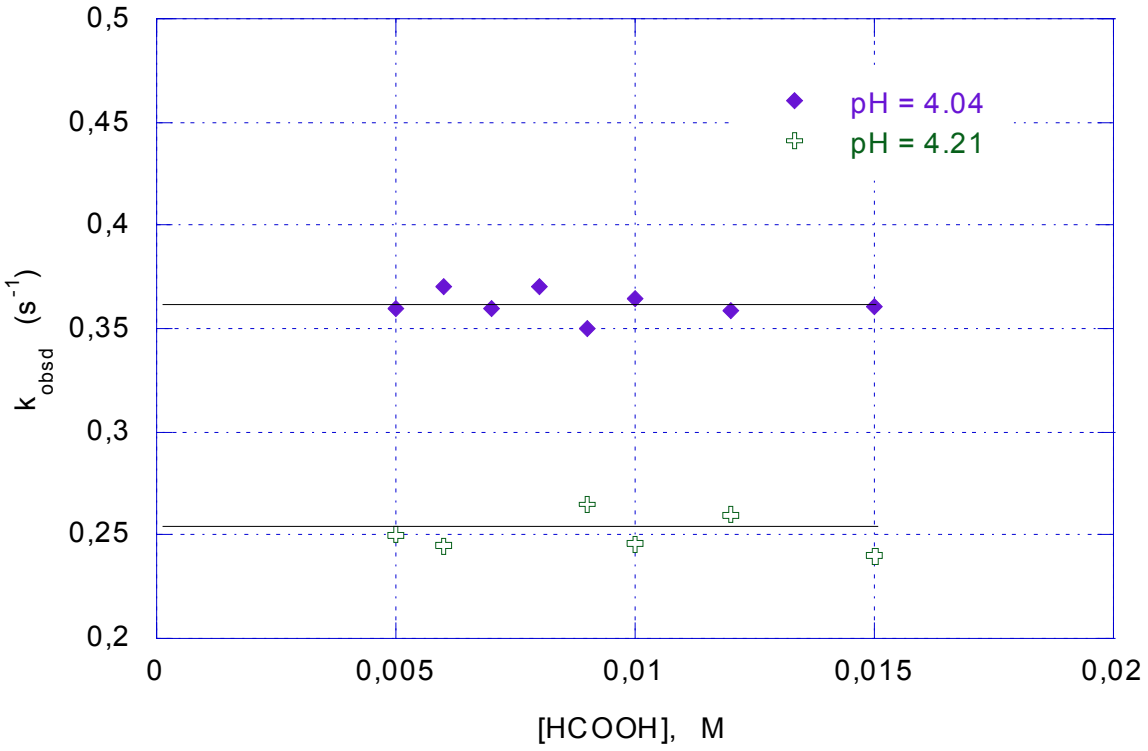

Figure S2 : Plot showing the lack of buffer dependence of k_{obsd} in formic acid buffers at pH 4.04 and 4.21 in the DNBSe system.

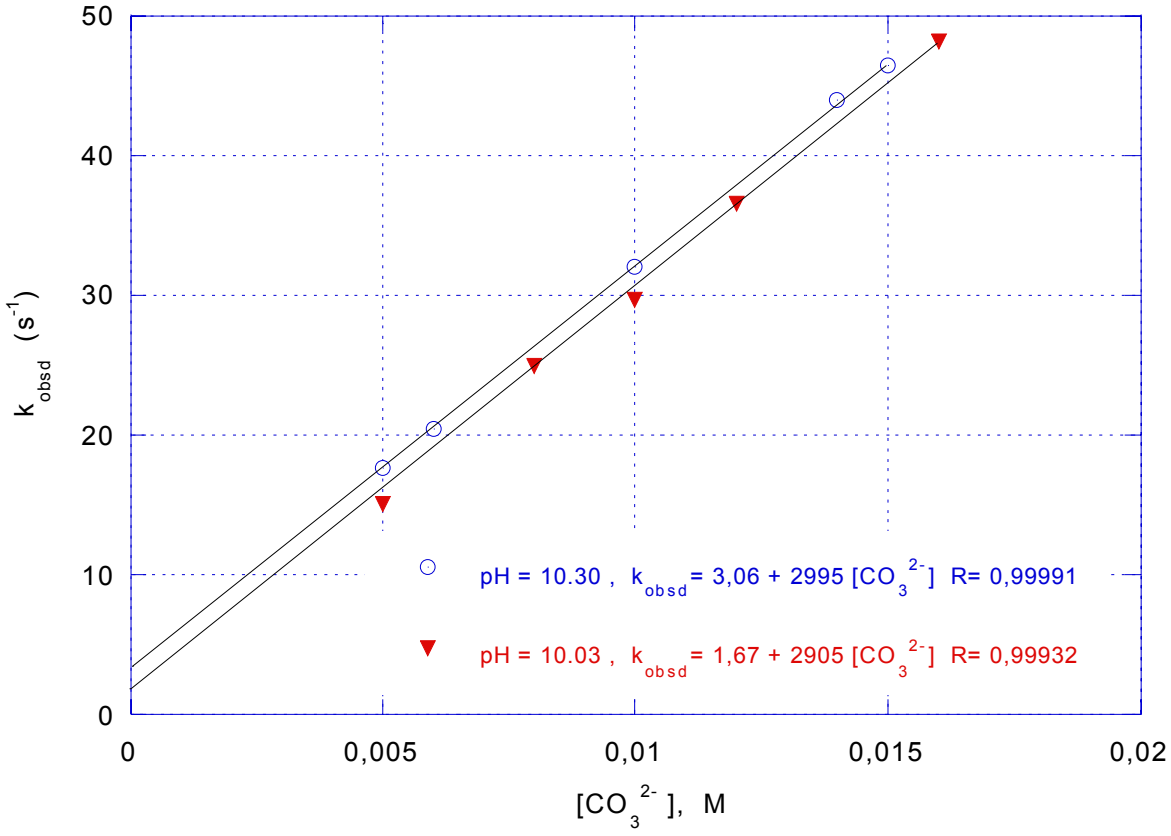

Figure S3 : Effect of carbonate concentration and pH on k_{obsd} for formation of the DNBZ adduct **C-2** in aqueous solution ; T = 25 °C, I = 0.2 mol dm^{-3} KCl.

Table S1. Observed first-order-rate constants, k_{obsd}, for formation and decomposition of the adduct **C-2** in water.[a]

pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}
1.12 [b]	12.67	7.27 [f]	0.032
1.34 [b]	7.73	7.53 [f]	0.038
1.82 [b]	2.58	7.83 [f]	0.052
2.12 [b]	1.23	8.38 [g]	0.31
2.34 [b]	0.73	9.30 [h]	0.46
2.82 [b]	0.19	9.73 [h]	1.55
3.48 [c]	0.087	10.03 [h]	3.05
3.74 [c]	0.058	10.30 [h]	4.80
3.97 [c]	0.040	11.15 [i]	26.9
4.40 [d]	0.029	11.45 [i]	58
4.70 [d]	0.026	11.65 [i]	98
5.00 [d]	0.024	11.75 [i]	118
6.00 [e]	0.024	12.05 [i]	155
6.28 [e]	0.024	12.35 [i]	600
6.58 [e]	0.025	12.53 [i]	926

(a) at zero buffer concentration; I = 0.20 mol dm^{-3}; T = 25°C;
(b)HCl solutions;
(c) Formate buffer;
(d) acetate buffer;
(e) cacodylate buffer;
(f) TES buffer;
(g) bicarbonate buffer;
(h) carbonate buffer;
(i) KOH solutions.

Table S2. Observed first-order-rate constants, k_{obsd}, for formation and decomposition of the adduct **C-3** in water.[a]

pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}
2.12 [b]	86.36	7.02 [f]	0.0068
2.42 [b]	42.05	8.12 [g]	0.0081
2.52 [b]	31.52	9.73 [h]	0.018
2.70 [b]	10.36	10.03 [h]	0.025
3.48 [c]	2.95	11.00 [i]	0.25
3.74 [c]	1.51	11.30 [i]	0.57
3.97 [c]	0.344	11.47 [i]	0.62
4.21 [c]	0.46	11.60 [i]	1.00
4.40 [d]	0.32	11.78 [i]	1.31
4.70 [d]	0.10	12.20 [i]	4.09
6.50 [e]	0.008	12.67 [i]	14.16

(a) at zero buffer concentration; I = 0.20 mol dm^{-3}; T = 25°C;
(b)HCl solutions;
(c) Formate buffer;
(d) acetate buffer;
(e) cacodylate buffer;
(f) phosphate buffer;
(g) bicarbonate buffer;
(h) carbonate buffer;
(i) KOH solutions.

Table S3. Observed first-order-rate constants, k_{obsd}, for formation and decomposition of the adduct **C-4** in water.[a]

pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}
2.12 [b]	163	8.12 [f]	0.0091
2.22 [b]	126	8.38 [g]	0.013
2.42 [b]	73	9.50 [h]	0.154
2.52 [b]	57.5	9.72 [h]	0.251
2.82 [b]	24.83	10.03 [h]	0.49
4.40 [c]	0.70	10.38 [i]	0.85
4.70 [c]	0.276	11.60 [i]	16.41
5.00 [c]	0.158	12.00 [i]	40.34
6.50 [d]	0.0062	12.20 [i]	73.66
6.72 [e]	0.0047	12.30 [i]	89.33
7.02 [e]	0.0041	12.48 [i]	136.3
7.83 [f]	0.0055	12.60 [i]	180.4

(a) at zero buffer concentrations; I = 0.20 mol dm^{-3}; T = 25°C;

(b)HCl solutions;

(c) acetate buffer;

(d) cacodylate buffer;

(e) phosphate buffer

(f) TES buffer;

(g) bicarbonate buffer;

(h) carbonate buffer;

(i) KOH solutions

Table S4: Selected ^{1}H nmr data for isoprene and 2,3-dimethylbutadiene Adducts of **2-4** and DNBF **1** in $CDCl_3$.[a)]

Compounds	H_5	H_7	H_{10}	H_{12}	H_{13}	H_{14}	H_{15}	H_{17}	CH_3
11a	7.57	4.22	2.67 2.32	5.49	3.14 2.81	-	-	-	1.77
11b	7.54	4.15	2.66 2.28	-	3.09 2.71	-	-	-	1.75 1.70
12a	3.90	4.19	2.76 2.45	5.34	2.85 2.41	3.21	5.43	2.15 1.93	1.71 1.66
12b	3.78	4.19	2.73 2.34	-	2.78 2.27	3.14	-	2.08 1.85	1.67 ; 1.65 1.60 ; 1.56
13a	7.71	4.39	2.76 2.41	5.44	3.16 2.61	-	-	-	1.77
13b	7.64	4.34	2.73 2.51	-	3.09 2.51	-	-	-	1.71
14a	3.97	4.14	2.88 2.67	5.23	2.88 2.31	3.22 3.02	5.39	2.23 2.03	1.66
14b	3.89	4.07	2.85 2.65	-	2.79 2.23	3.21 2.99	-	2.26 1.95	1.62 ;1.56
16a	4.03	4.07	2.52	5.27	2.52	3.31 2.94	5.41	2.2	1.69 ; 1.66
16b	3.86	4.06	2.75	-	2.80 2.39	3.22 2.87	-	2.10	1.62 ; 1.60 1.58 ; 1.56
18a	3.99	4.12	2.68	5.34	2.82	3.50 2.59	5.45	2.27	1.71 ; 1.68
18b	4.10	3.91	2.68	-	2.72 2.62	3.40 2.65	-	2.22	1.67 ; 1.65

a) δ in ppm, internal reference Me_4Si.

Table S5: Selected ^{13}C nmr data for isoprene and 2,3-dimethylbutadiene Adducts of **2-4** and DNBF **1** in $CDCl_3$.[a)]

Compounds	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	CH_3
11a	141.1	137.6	87.3	33.1	109.7	143.5	29.1	134.4	115.5	34.6	-	-	-	-	22.6
11b	141.1	137.3	88.2	33.2	109.9	143.4	30.6	126.5	121.6	40.1	-	-	-	-	18.8 ; 18.1
12a	86.3	42.2	92.6	30.6	112.3	149.6	28.1	135.0	116.3	32.2	33.5	115.9	131.7	28.5	22.6 ; 22.6
12b	86.8	43.5	93.9	30.4	112.4	149.5	29.4	126.2	123.2	38.0	38.9	122.0	123.2	30.5	18.6 ; 18.3 18.1
13a	143.2	138.4	88.0	33.3	154.3	144.2	30.2	133.8	115.1	34.6	-	-	-	-	22.8
13b	142.0	138.0	88.8	33.4	153.3	143.3	32.0	125.5	121.0	39.1	-	-	-	-	18.8; 18.4
14a	86.0	42.0	91.3	30.9	153.7	148.1	32.4	133.5	115.4	31.1	35.7	116.3	133.5	27.6	22.3 ; 22.5
14b	86.6	43.5	92.4	30.8	153.9	148.2	33.4	125.3	124.9	36.8	41.8	121.3	123.3	29.7	18.9 ; 18.4 18.2
16a	92.1	41.6	89.4	37.5	160.9	152.4	31.9	132.7	115.6	33.2	35.2	116.8	123.9	27.9	22.5 ; 22.2
16b	92.8	42.7	89.8	36.9	160.8	152.4	34.0	124.4	121.2	37.2	41.0	123.1	124.8	29.6	18.2 ; 18.5 18.0 ; 18.3
18a	91.7	39.7	92.7	41.7	163.7	157.0	34.6	132.3	115.9	32.5	34.3	117.2	133.5	27.3	22.7 ; 22.2
18b	92.8	41.3	93.5	41.6	164.0	157.2	35.4	124.2	124.0	38.0	40.6	124.0	124.8	29.5	18.9 ; 18.5 18.0 ; 18.3

a) δ in ppm, internal reference Me_4Si.

Table S6: ^{1}H nmr data for the cyclopentadiene and cyclohexadiène adducts of **2-4**, **5a** and DNBF **1** in $CDCl_3$. in $CDCl_3$.[a)]

Compounds	H_5	H_7	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}	H_{15}	H_{16}	H_{17}	H_{18}	H_{19}	Pi
9	3.49	4.06	3.98	5.77	5.95	6.21	2.41 2.16	4.06	6.38	6.69	3.49	1.80 1.18	-
10	3.49	4.06	3.98	5.77	5.95	6.21	2.41 2.16	4.06	6.38	6.69	3.49	1.80 1.18	9.23
19	3.55	4.35	3.89	5.79	5.95	6.19	2.34 2.00	4.00	6.38	6.69	3.52	1.74 1.00	-
20	3.52	4.31	3.90	5.77	5.94	6.15	2.19 1.98	3.98	6.39	6.64	3.50	1.64 0.96	-
21	8.02	4.11	3.46	6.67	6.37	3.78	1.18 1.39	1.39 1.83	-	-	-	-	-
22	8.00	4.46	3.35	6.72	6.35	3.82	1.16 1.46	1.46 1.87	-	-	-	-	-
23	7.38	4.40	3.47	6.67	6.29	3.64	1.16 1.44	1.44 1.57	-	-	-	-	-
24	7.29	4.37	3.50	6.65	6.28	3.63	1.16 1.45	1.45 1.63	-	-	-	-	-
25	7.56	4.36	3.65	6.72	6.59	3.65	0.86 1.36	1.36 1.77	-	-	-	-	9.26

a) δ in ppm, internal reference Me_4Si.

Table S7: ^{13}C nmr data for the cyclopentadiene and cyclohexadiène adducts of **2-4**, **5a** and DNBF **1** in $CDCl_3$.[a)]

Adducts	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	Pi
9	91.27	47.54	121.82	32.17	111.35	152.69	36.61	91.67	127.52	139.36	34.60	54.56	134.27	141.90	46.11	46.24	-
10	93.2	49.0	123.1	33.5	124.4	145.7	38.4	93.0	128.3	140.4	35.3	55.2	135.4	142.3	47.4	47.1	124.4 ;128.3 147.2 ; 150.4
19	90.1	47.6	123.2	32.7	152.2	150.7	43.0	91.8	127.0	140.0	35.2	55.2	134.6	141.2	46.4	46.6	-
20	94.5	54.5	124.7	38.4	157.0	154.7	43.2	91.8	127.0	140.0	35.0	54.8	135.2	140.7	46.3	46.3	-
21	141.4	137.8	93.8	37.1	110.8	146.0	30.18	136.4	131.5	40.5	21.2	18.4	-	-	-	-	-
22	137.7	137.1	92.3	59.3	153.5	143.6	36.7	136.9	130.9	40.4	21.5	18.2	-	-	-	-	-
23	147.8	131.2	94.2	45.1	157.0	154.7	36.7	136.6	130.1	39.6	20.4	18.2	-	-	-	-	-
24	149.2	130.7	94.0	45.1	163.1	150.2	33.2	136.5	130.0	36.7	20.5	18.3	-	-	-	-	-
25	141.1	136.4	93.7	36.3	122.8	136.1	29.2	133.8	130.2	39.7	20.6	18.1	-	-	-	-	124.5 ;124.7 1 46.5 ; 148.7

a) δ in ppm, internal reference Me_4Si.