Effect of pressure on the low-temperature reaction of ethylene with N_2O_4

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Experimental details

IR-spectra were measured using Bruker IR spectrometer.

Prior to the experiments, the autoclave (75 ml) was checked for leaks, heated up to 70 ºC and evacuated to 10 Torr. Then the autoclave was blown through with dry argon to remove oxygen or moisture traces, cooled down to room temperature and put into a Dewar vessel filled with isooctane. The autoclave was further cooled down to –8 — –3ºC in three stages by adding liquid nitrogen. Liquid dinitrogen tetroxide (N_2O_4) was injected by a gas-proof syringe with a cooling mesh *via input 2* (Figure S1). Then the autoclave was cooled down to –95 — –85ºC for ethylene injection. A desired amount of ethylene was pressurized into a calibrated volume tube connecting *Valves 4* and *3b*. The amount of ethylene was calculated taking into account equilibrium pressure reached after *Valve 3b* is opened to connect the autoclave with the calibrated volume tube. Desired initial pressure inside the autoclave was adjusted by pressurized argon filling. After this step, the Dewar vessel was removed and the autoclave was exposed to a heat ambient. To reduce an impact of natural convection on the heating, the autoclave was placed into a stainless vessel (see Figure S1). The autoclave was then depressurized using *Valve 3* when the ambient heating ended. The argon containing the reaction products was directed to the cooled trap (–40ºC) to condense the gaseous products if any. Calorimetric technique was used to monitor chemical reactions and phase changes. Variations of the temperature inside the autoclave were monitored using Pt-sensor placed near the Teflon insert bottom, the pressure inside the autoclave was monitored too. Time resolution of the temperature and pressure measurements is 1 second. Pressure resolution is 0.1 bar.
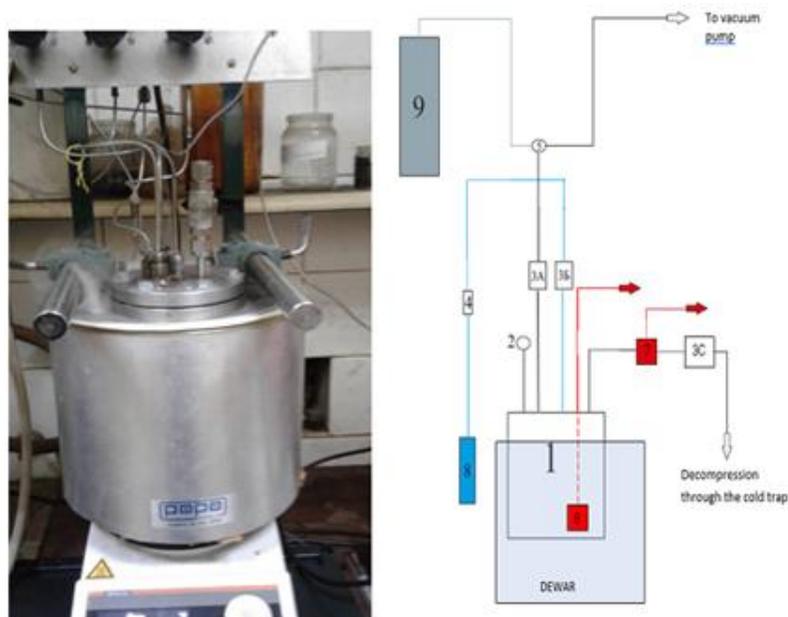
Figure S1 Scheme and photo of the experimental setup. 1 – Reactor (autoclave), 2 – N_2O_4 injection valve, 3 – Cut off valves, 4 – Control valve, 5 – Flow direction switch, 6 – Temperature sensor, 7 – Pressure sensor, 8 – Ethylene cylinder, 9 – Argon cylinder.

Table S1 Details of the experiments

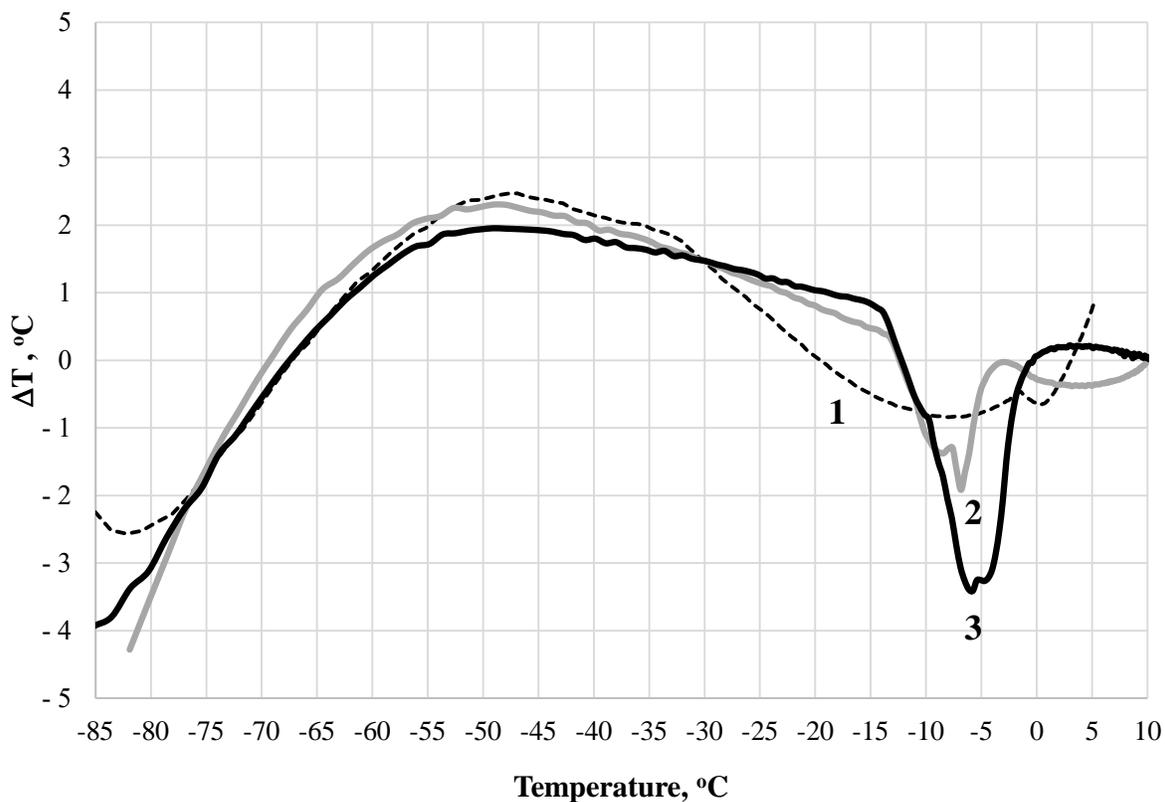| #	Parameter	N_2O_4 + Ar 10 bar	C_2H_4 + Ar 10 bar	N_2O_4 + C_2H_4 + Ar 10 bar	N_2O_4 + Ar 30 bar	C_2H_4 + Ar 30 bar	N_2O_4 + C_2H_4 + Ar 30 bar
1	N_2O_4 quantity, mmol	1.6	—	1.6	1.6	—	1.6
2	Temperature of N_2O_4 injection, ºC	–3	—	–3	–3	—	–3
3	C_2H_4 quantity, mmol	—	4.2	4.2	—	4.2	4.2
4	Temperature of C_2H_4 injection, ºC	—	–85	–85	—	–85	–85
5	Pressure after C_2H_4 injection, bar	1.5	1.5	1.5	1.5	1.5	1.5
6	Temperature of Ar injection, ºC	–90	–90	–90	–90	–90	–90
7	Pressure after Ar injection, bar	10	10	10	30	30	30
8	Final pressure, bar	20	20	20	40	40	40

Figure S2. Temperature variations, fit curve is the reference: (*1*) — blank experiment: Ar only, N_2O_4 + Ar mixtures: (*2*) — 10 bar, (*3*) — 30 bar.
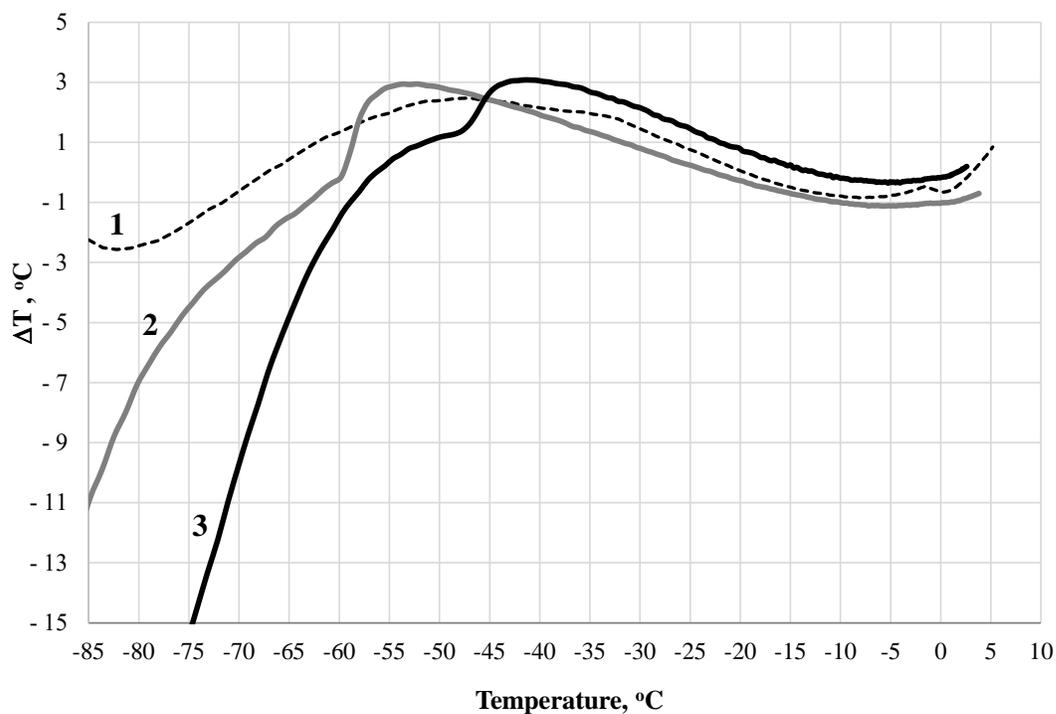

Figure S3. Temperature variations, fit curve is the reference: (*1*) — blank experiment: Ar only, C_2H_4 + Ar mixtures: (*2*) — 10 bar, (*3*) — 30 bar.
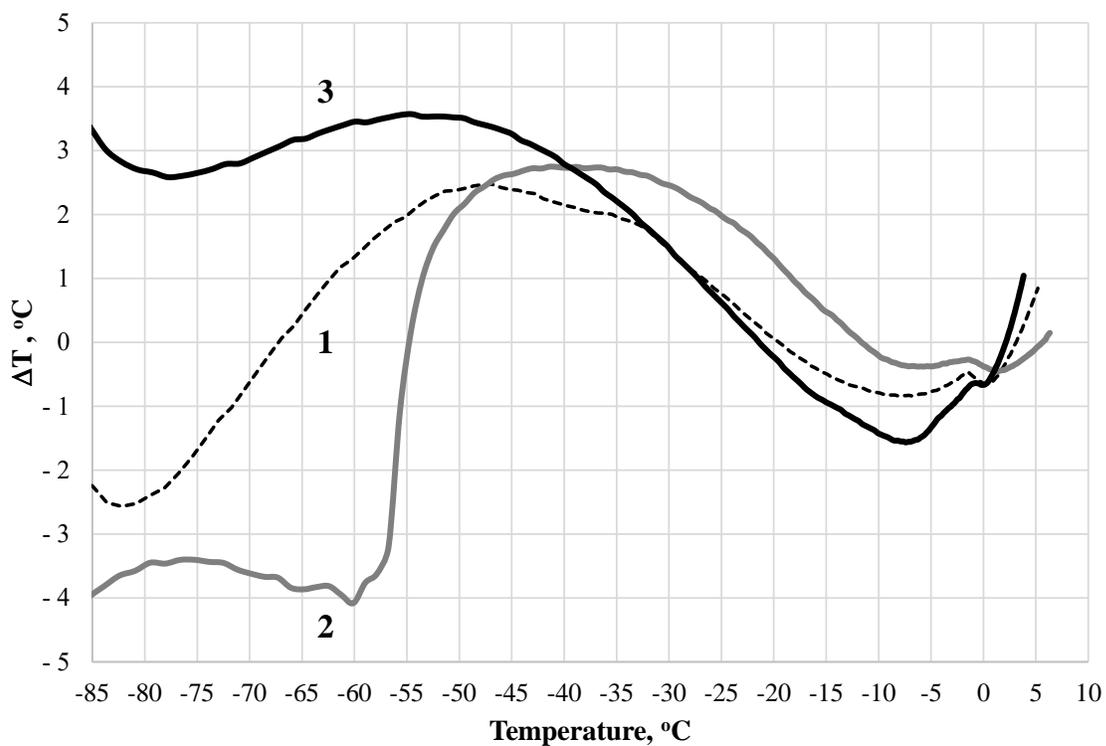
Figure S4. Temperature variations, fit curve is the reference: (*1*) — blank experiment: Ar only, $C_2H_4 + N_2O_4 + Ar$ mixtures: (*2*) — 10 bar, (*3*) — 30 bar.
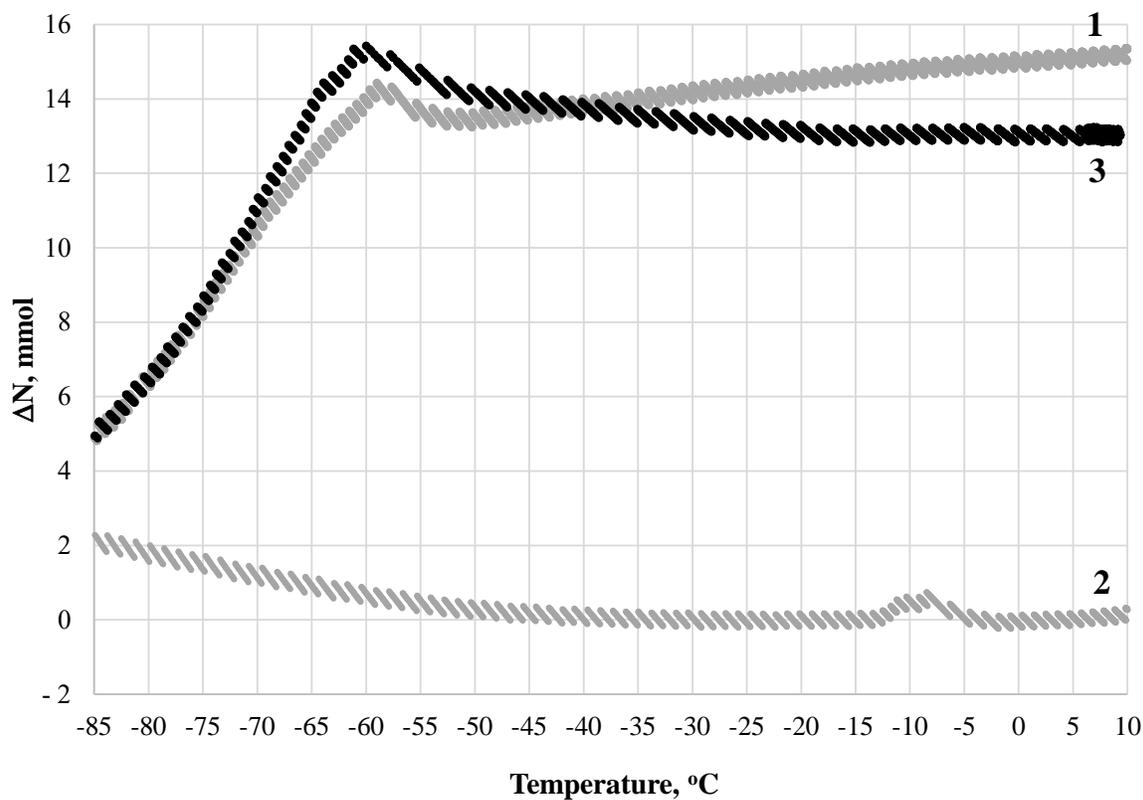

Figure S5. Variations of the autoclave gas phase amount (ideal gas law), $P = 10$ bar, mixtures (*1*) — $C_2H_4 + Ar$, (*2*) — $N_2O_4 + Ar$, (*3*) — $C_2H_4 + N_2O_4 + Ar$.

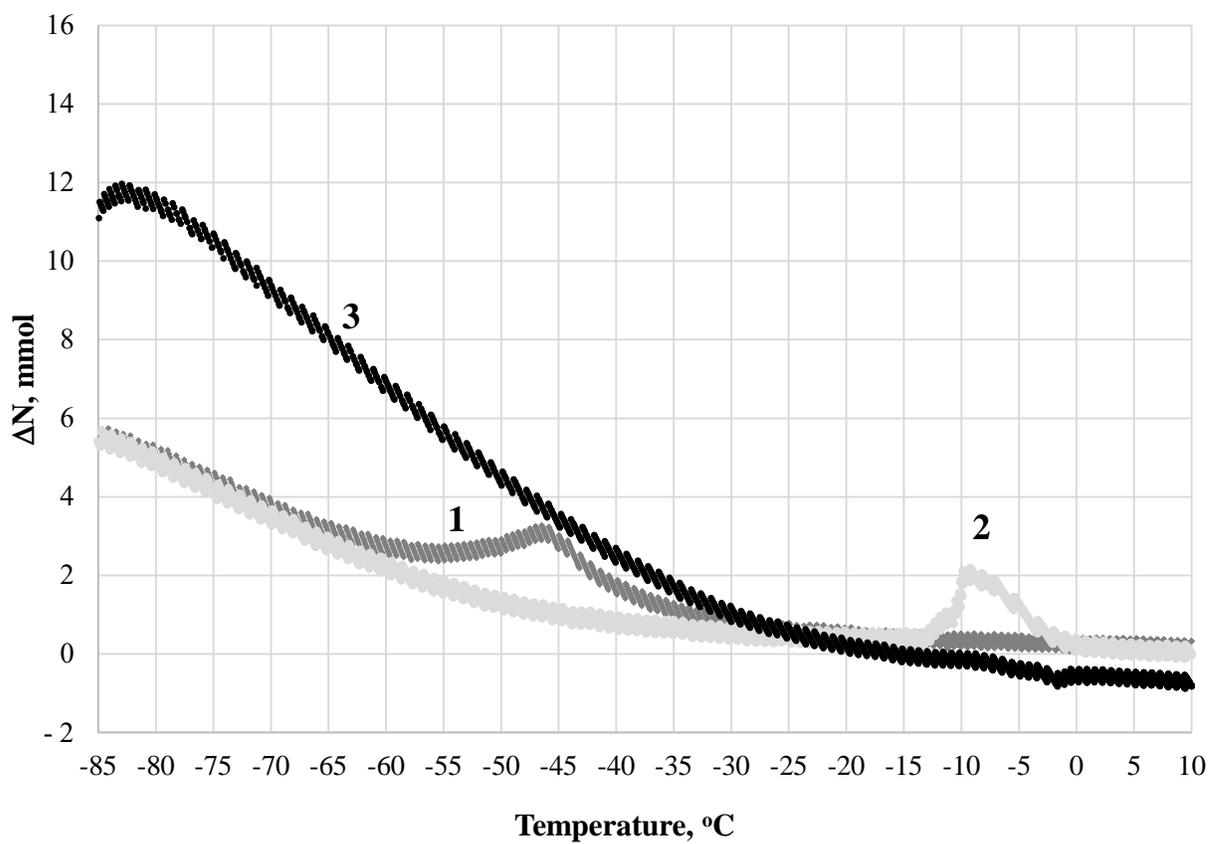**Figure S6.** Variations of the autoclave gas phase amount (ideal gas law), $P = 30$ bar, mixtures (1) — $C_2H_4 + Ar$, (2) — $N_2O_4 + Ar$, (3) — $C_2H_4 + N_2O_4 + Ar$.